Systematic Development for High Performance Fluoropolymer Materials and Applications

Dissertation

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Content

List of frequently used symbols and abbreviations

ΔH	enthalpy of fusion of the heating of sintered products
ΔH_C	heat of crystallization
ΔH^f	heat of fusion
ΔH_{f1}	enthalpy of fusion, 1.heating
ΔH_{f2}	enthalpy of fusion, 2.heating
$\Delta H^f{}_0$	heat of fusion of the 100 % crystalline sample
E	activation energy
E*	complex modulus
E´	storage modulus
E´´	loss modulus
ε	strain
M_n	number average molecular weight
M_w	weight average molecular weight
P	load
P_N	degree of polymerization
R	gas constant
t	time
T_{0m} (X)	equilibrium melting point
tan δ	loss factor
T_G	glass transition temperature
T_M	melting temperature
T_{m1}	melting temperature, 1. heating
T_{m2}	meting temperature, 2. heating
v	velocity
X^C	degree of crystallinity
X_{C0}	weight degree of crystallinity
ΔG	free enthalpy
ΔS	entropy
ρ	denity
σ	stress

42CrMo4	high grade steel
ABS	acrylonitrile butadiene styrene copolymers
ABS/PC	acrylonitrile butadiene styrene / polycarbonate
AFFF	arqueous film forming foam
AFFF-AR	arqueous film forming foam
Arom.Pol.	aromatic polyimide

ASA	acrylonitrile styrene acrylate copolymers
BET	Brunauer–Emmett–Teller
C	carbon
Ca	calcium
CF	carbon fiber
CFC	chlorofluorocarbon
CM	crystallite melting area
COF	coefficient of friction
DI	deionized
DMA	dynamic mechanical analysis
DMTA	dynamic mechanical thermal analysis
DR	decomposition range
DSC	differential scanning calorimetry
DTA	differential thermal analysis
ECTFE	ethylene chlorotrifluoroethylene
E-mobility	electromobility
E-PTFE	emulsion - polytetrafluoroethlyene
ETFE	ethylene tetrafluoroethylene copolymer
F	fluorine
F-CSM	chlorosulfonated synthetic rubber
FDA	Food and Drug Administration
FE	fluorinated ethylene
FEP	fluorinated ethylene-propylene
FFFP	filmbuilded fluor protein foaming agents
FKM	fluorocarbon rubber
FT-IR	fourier transform infrared spectrometer
FTP	fracture transition plastic
H	hydrogen
HFPO	hexafluoropropylene oxide
HRC	Rockwell
LCP	liquid crystal polymer
MoS_2	molybdenum disulfide
N_2	nitrogen
O	oxygen
p.a.	pro analysis
PA	Polyamide
PA1012	Polyamide 1012
PA12	Polyamide 12
PA6	Nylon 6
PAI	polyamide-imide
PAR	polyarylate
PBT	polybutylenterephthalate
PBT/PC	polybutylene terephthalate / polycarbonate
PC	polycarbonate

PCTFE	polychlorotrifluoroethylene
PE	polyethylene
PEEK	polyetheretherketone
PEEKK	polyetheretherketoneketone
PEI	polyetherimide
PEK	polyetherketone
PET	polyethylene terephthalate
PEVE	perfluoroethylvinylether
PFA	perfluoroalkoxy polymers
PI	polyimide
PMVE	perfluoromethylether
POM	polyoxymethylene
PP	polypropylene
PPME	polyphosphomannan
PPS	polyphenylensulfide
PPS	polyphenylene sulfide
PPSO2	polyphenylene sulfone
PPSU	polyphenylsulfone
PPVE	perfluoropropylvinyl ether
PS	polystyrene
PSD	particle size distribution
PSU	polysulfone
PTFE	polytetrafluoroethlyene
PTFE-TFM	modified PTFE of Dyneon GmbH
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
S	sulfur
SAN	styrol-acrylnitril-copolymere
SB	styrene / butadiene
S-PTFE	Suspension - polytetrafluoroethlyene
SR	softening range
SSG	standard specific gravity
TFE	tetrafluoroethylene
TGA	thermogravimetric analysis
THV	terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride
TiO_2	titanium dioxide
VF_2	vanadium fluoride

All other symbols and abbreviations are defined on the first appearance in the text.

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Abstract

The aim of the work includes several steps. After the material characterization of the PTFE itself, the processing technologies and the tribological characterization of compounds, a revision of suitability has to be done and the correlation between the filler and the processing technology must be respected. If the suitability or the correlation is not fitting for the favoured application it is recommended to return to the material characterization of the PTFE to find the best solution. By using this systematic way the optimized material for nearly every application can be found. Only by a broad knowledge of the different PTFE materials, their properties and the processing technologies in combination with the manufacturing process enables to find the material and process solution. Depending on the targeted applications the required performance profile may be different. In this work all important chemical, physical and mechanical influences are determined and analyzed. The study of mechanical and thermal behaviour of these materials gives a better unterstanding of the relationship between molecular weight, molecuar weight distribution, particle composition and material characteristics.

By utilising these processes the following conclusions are made:

- The particle size and the weight percentage of the d_{10}-fraction of the material are specific for each material type. The increased specific surface enables an improved coalesence of the particles. In addition, a rough surface compared to a smooth one generates a better surface contact during moulding. Producing compounds will be done with low flow material because due to the lower particle size the filler distribution is more homogenious.
- In difference to Standard PTFE, modified PTFE has a reduced molecular weight, a reduced cold flow, enhanced mechanical properties and a better melting behaviour during sintering as a consequence of the reduced melting viscosity.
- PTFE processing is not critical for local pressure variations inside the mould. But lower moulding pressure generates higher shrinkage during sintering.
- Compounds with low phyiscal strength are not acceptable for high strain. It can be said, that low elongation is a disadvantage for the manufacturing and assembly process and recovers the danger of crack formation at impact load. A low shrinkage behaviour during sintering is advantageous for the manufacturing of stress-relieved components.

After testing the samples on the different conditions the best results are obtained for material No. 7 which is a compound composed of Standard PTFE + 15% PPS + 10% Carbon Coke + 2%MoS_2. This compound generates a high wear resistance and a reduced coefficient of friction. The comparison of mechanical and tribological performance of Standard PTFE, modified PTFE and PTFE compounds show the potential of this materials for industrial applications. In general, the mechanical properties of PTFE play an important role for

material selection for any application and can potentially provide new solutions on the fluoropolymer market.

Kurzzusammenfassung

Das Ziel der vorliegenden Arbeit ist mehrstufig gegliedert. Nach der Materialcharakterisierung des PTFE, der Einbeziehung der Verarbeitungstechnologie und der tribologischen Charakterisierung der Compounds, wird eine Prüfung auf die Verwendbarkeit durchgeführt. Zusätzlich wird der Zusammenhang zwischen den Füllstoffen und der Verarbeitungstechnologie betrachtet. Sollte sich bei der angestrebten Anwendung keine Verwendbarkeit oder kein logischer Zusammenhang ergeben, ist es empfehlenswert durch eine erneute Materialcharakterisierung einen anderen, besseren Lösungsansatz zu finden. Durch das Einhalten dieser Systematik ist es möglich das optimale Material für nahezu jede Anwendung zu identifizieren. Eine umfassende Kenntnis der verschiedenen PTFE Materialien, ihren Eigenschaften und die Verarbeitungstechnologien, in Kombination mit dem Polymerherstellprozess, ermöglichen eine vollständige Lösungsfindung. Die jeweiligen Anforderungsprofile sind, abhängig von der angestrebten Anwendung, immer unterschiedlich zu betrachten. In dieser Arbeit findet die Untersuchung und Analyse aller wichtigen chemischen, physikalischen und mechanischen Einflüsse statt. Insbesondere das mechanische und thermische Materialverhalten geben einen umfangreichen Aufschluss über die Beziehungen zwischen Molekulargewicht, Molekulargewichtsverteilung, dem Aufbau der Partikel und den Materialeigenschaften.

Die Untersuchungen lassen folgende Schlussfolgerungen zu:

- Für jeden Materialtyp sind die Partikelgröße und der Gehalt an Feinanteilen, der d_{10}-Fraktion, kennzeichnend. Die vergrößerte spezifische Oberfläche des Pulvers ermöglicht ein verbessertes Verschmelzen der Partikel. Darüber hinaus erzeugt eine unregelmässige Oberfläche im Gegensatz zu einer Glatten einen besseren Oberflächenkontakt während des Pressvorgangs. Zur Herstellung von Compounds wird nicht rieselfähiges Material verwendet, da aufgrund der geringeren Partikelgröße die Verteilung der Füllstoffe homogener ist.
- Im Gegensatz zu Standard PTFE ist das modifizierte PTFE charakterisiert durch ein geringeres Molekulargewicht, einen reduzierten Kaltfluss, verbesserte Verankerung von Füllstoffpartikeln und ein besseres Schmelzverhalten während des Sinterns, eine Konsequenz der verringerten Schmelzviskosität.
- Das Verarbeiten von PTFE bei verschiedenen Pressvariationen im Werkzeug ist unkritisch. Allerdings bedeutet ein niedriger Pressdruck mehr Schrumpf während des Sinterns.
- Compounds mit niedrigen Festigkeitseigenschaften sind für Anwendungen mit höherer Belastungen nicht geeignet. Daher ist eine geringe Bruchdehnung für den Verarbeitungsprozess nachteilig und erhöht die Gefahr des Materialversagens bei Stoßbelastung. Ein niedriges Schrumpfverhalten während des Sinterns ist vorteilhalt für die Herstellung von spannungsarmen Komponenten.

Nach Abschluss der Versuchsreihe ergaben sich die besten Ergebnisse für Material Nr. 7, welches ein Compound, basierend auf Standard PTFE + 15% PPS + 10% Harte Kohle + 2%MoS_2 ist. Dieses Compound zeichnet sich durch einen geringen Verschleiß und einen niedrigen Reibwert aus. Der Vergleich der mechanischen und tribologischen Eigenschaften von Standard PTFE, modifiziertem PTFE und PTFE-Compounds zeigen das Potenzial dieses Materials auf industrielle Anwendungen. Grundsätzlich spielen die mechanischen Eigenschaften des PTFE eine wichtige Rolle für die Materialauswahl für jede Anwendung und können potenziell neue Lösungen für den Fluorpolymermarkt liefern.

1 Introduction

Polymer materials are offering a wide range of properties at a low density compared to metals, leading to high specific values (i. e. strength/density) making them applicable to advanced lightweight applications. [4] Relatively low-cost and automated manufacturing processes are additional benefits. For those reasons, polymer materials today can be found in almost every area of daily life. [5]

High molecular, organic based materials are used by humans since a long time in textiles prepared by natural fibers, wood and lether. The cellulose was the first indicator for the aimed transformation of natural materials into plastics – so called polymer materials. This began in the early 19th century with the modification of cellulose. [1] Polymer materials and plastics are products of research and development and, as can be seen in figure 1-1, the virtual plastic period first effectively started in the 20th century. Although in the nineteen-twenties the scientific basics were generated. [2]

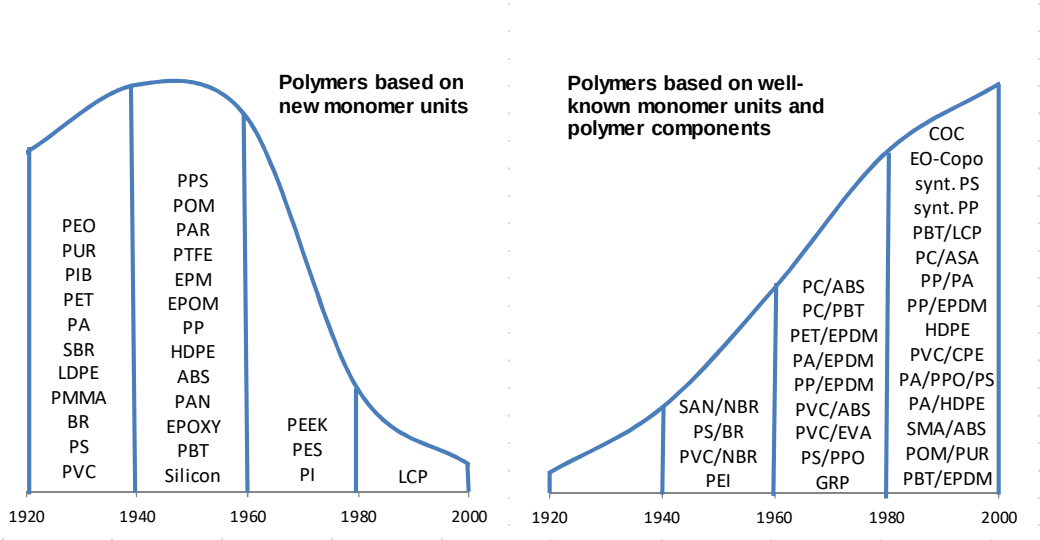


Figure 1-1: A chronology of the discovery of polymers and their modifications [56]

30 – 40 different polymer types are the base for the industrial important plastics, which are provided in 13.000 placements under 25.000 trade names. For polymers there can be made a differentiation into three groups, according to their applications, prices and quantities:

- Commodity plastics comprice thermoplastic, which are produced in big quantities, e.g. PVC, PE, PP and styrene polymer (PS, SB).
- In comparison to commodity plastics, engineering plastics perform through enhanced thermal and mechanical strength. They can be used for more demanding applications and complex loading conditions. Examples for this kind of plastics are PA, POM, PC, PET, PBT and styrene polymere (ABS/ASA, SAN), as well as blends (ABS/PC and PBT/PC).

- The third group are the high performance plastics, which are technical plastics with superior properties especially regarding thermal and mechanical applications. In this group there can be named fluoropolymers (PTFE, Fluorothermoplastics and Fluoroelastomers), polyether ketone (PEK,PEEK, PEEKK), polyimides (PI, PAI, PEI), polyphenylene sulfide (PPS), liquid-crystalline polymers (LCP) and aramide fibre and polysulfone (e.g. PSU, PPSU, PAR).

Most of these materials can be found in figure 1-2. In the group of FTP materials like PFA, FEP, ETFE, PVDF, ECTFE or THV are summarized. Depending on which continuous service temperature is required, a distinction is made between standard plastics, which are used up to 100°C, and engineering plastics for continuous service temperatures up to 150°C. Applications above 150 °C are covered by high performance plastics.

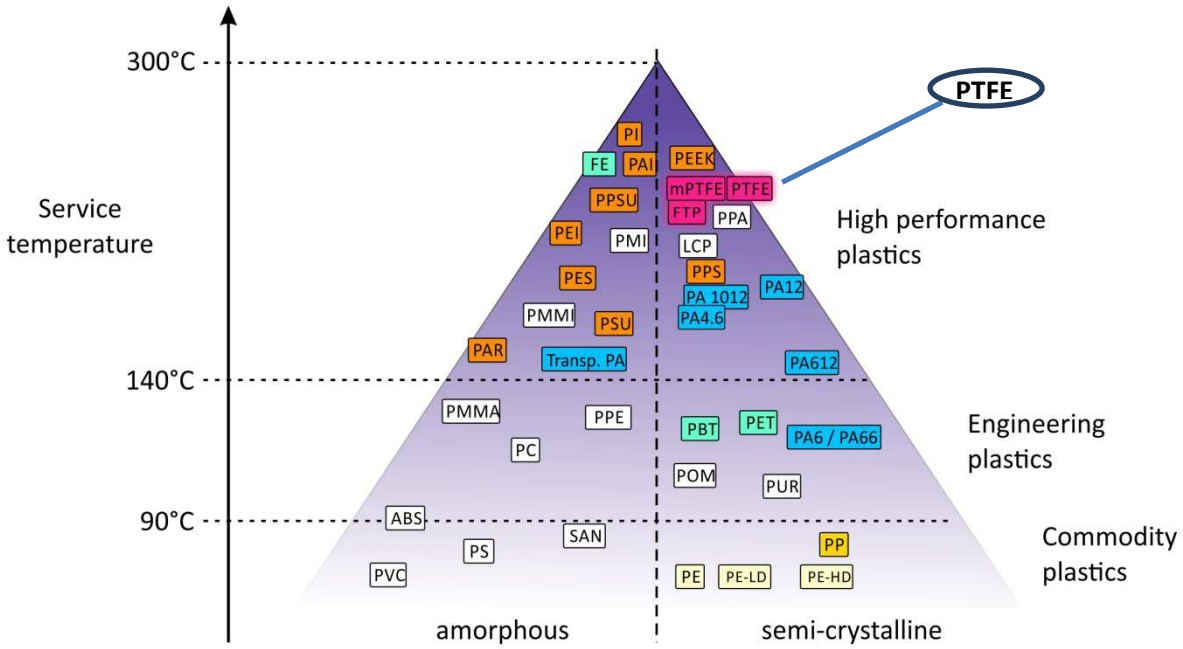


Figure 1-2: Positioning of fluoropolymers and classification of plastics on the basis of amorphous / semi crystalline regions and their continuous service temperature [8]

Legend:

PI	Polyimide	**PC**	Polycarbonate	**PA 4.6**	Polyamide
PAI	Polyamide-imide	**PS**	Polystyrene	**PA612**	Polyamide
PPSU	Polyphenylsulfone	**SAN**	Styrol-Acrylnitril-Copolymere	**PBT**	Polybutylenterephthalate
PEI	Polyetherimide	**PEEK**	Polyetheretherketon	**PET**	Polyethylene terephthalate
PMI	Polymethacrylimide	**mPTFE**	modified Polytetrafluoroethylene	**PA6/PA66**	Polyamide
PES	Polyethersulfon	**PTFE**	Polytetrafluoroethlyene	**POM**	Polyoxymethylene
PMMI	Polymethacrylmethylimide	**PPA**	Polyphthalamide	**PUR**	Polyurethane
PSU	Polysulfone	**LCP**	Liquid-crystalline polymer	**PE**	Polyethylene
Transp. PA	Polyamide-imide	**PPS**	Polyphenylensulfide	**PE-LD**	Polyethylene - Low Density
PMMA	Polymethylmethacrylat	**PA 1012**	Polyamide	**PE-HD**	Polyethylene - High Density
PPE	Polyphenylenether	**PA 12**	Polyamide		

The trend of plastic developments in processing can be determinded into four points:

- Improvement of diversification, more deep quality in order to conform with specific requirements, like service temperature, especially for commodity plastics, thus new high performance PAs move from technical polymers to high performance polymers (PA12, PA1012)
- Progress in process technologies, such as multi-component injection moulding, co-extrusion and blow moulding
- Increase and distribution of knowledge, especially know-how on product blends, special focus on homogenious compound blending
- New products with better sustainability, ressource protection and energy efficiency [2]
- Multifunctionality (specific applications)

One very important material is the high performance plastic PTFE, as can be seen in figure 1-3 below, the global market for fluoropolymers in 2014 had three major application areas in industrial processing, electrical and electronics and automotive and aerospaces. Also in healthcare and constructions they were found. Up to now, PTFE materials, especially with its modifications, is not studied very well.

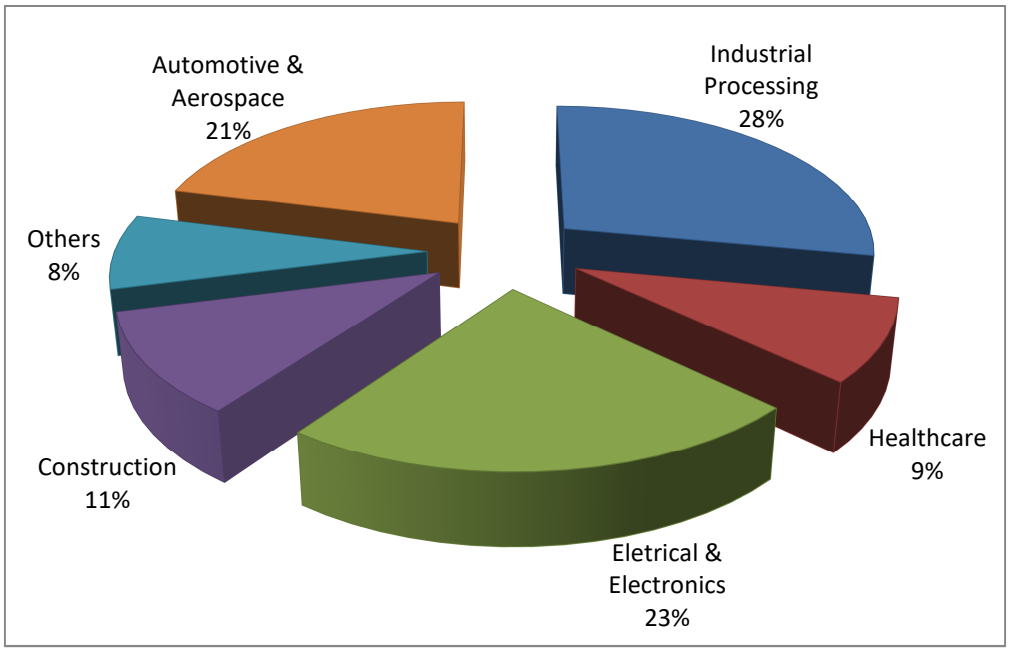


Figure 1-3: Global fluoropolymer market by end use, 2014 [3]

On April 6th 1938 Roy Plunkett, a research chemist at DuPont, discovered polytetrafluoroethylene (PTFE). He was rather working on synthesizing new forms of another DuPont product and they tested reactions using pressurized cylinders of tetrafluoroethylene (TFE). He used a filled cylinder with TFE, but this cylinder failed to discharge when the valve was opened. After discarding the cylinder, which was too heavy to be empty, they opened and found a white powder. For studying this substance Plunkett stopped initially his refrigerant research and discovered that the gas has polymerized in the cylinder. But more important he devised a way to convert the TFE into PTFE by polymerization in the lab. In the following

years, 1941 PTFE had been patented and was firstly brand named Teflon®. In 1946 PTFE product was being used to produce machine parts for military and industrial applications. By the 1960s PTFE started its life in nonstick cookware and today it is also implemented in a wide range of industries from aerospace to pharmaceuticals in every country worldwide. Within the years the use of PTFE has increased in following applications: automotive, medical, household, food packaging, textiles, personal care and industry. PTFE vascular grafts (used for replacing small arteries with diameter 6 to 8 mm or less) are used in the medical implants in bodies, because porous PTFE gets blood thight due to cell ingrowth.

This means more than 80 years PTFE is placed at an outstanding position in the industry because of its unique properties. The molecular weight of PTFE is approximately 10^8g/mol. [9] In addition to the above mentioned general benefits of plastics, PTFE also has:

- an excellent chemical resistance
- a wide temperature application range with -250°C to + 250 °C
- excellent non-stick properties
- a low coefficient of friction
- good sliding properties
- good electrical insulating resistance.

Over the last 40 years the yearly increase was about 3 – 5%. Now there is a worldwide usage of about 144.000t a year. About two-thirds of them is Suspension (S) - PTFE material, one-third Emulsion (E) - PTFE material. Communication and digitalisation are driven by PTFE with its low dielectric constant of 2.1 and its negligible damping of GHz frequencies. Especially in E-mobility fluoropolymers namely PVDF can be found in key applications in storage components like batteries and fuel cells, because of its unique properties. [7]

PTFE with its nonstick surface qualities is, as already mentioned, also used in household goods, for example cookware, bakeware and small electronics. In carpet fibers and paints it is used to generate strain resistance qualities and it is also used to coat light bulbs to make them shatter resistant. In the automotive area PTFE is found in windshield wiper blades, oil filters, and lubricants because of its low coefficient of friction. It is also found in paint coatings and fabric coatings in automobiles. The use of PTFE in coatings and certain other food contact applications is permitted under FDA regulations. Clothing uses PTFE as a fabric protector. Gore-Tex® has a proprietary mechanical heating and stretching process for using PTFE in clothing to allow a breathable watertight fabric. PTFE is also present in the personal care area. It is used in nail polish, hair styling tools and eyeglass lens coating for both anti-reflective and scratch resisting qualities. [6]

In the group of fluoropolymers, the fully fluorinated high performance plastic polytetrafluoroethylene (PTFE) is the fluoropolymer which is most frequently used because of its extraordinary range of properties combined with its highly economical price-performance ratio.

PTFE is an unbranched, linear-structured and semi-crystalline polymer built by the elements fluorine and carbon. The reason for its excellent properties is its chemical structure. The carbon-fluorine bond with its bonding energy of 460 kJ/mol is the strongest binding known in organic chemistry and can be separated only under extreme conditions. [10] Furthermore, the fluorine atoms shield the carbon skeleton effectively from any chemical attacks.

However, characteristic deficits of classic PTFE are, among other things, a difficult processing on plastic weldability as well as the deformation under load, which is also referred to cold flow. These disadvantages were overcome by the development of the 2nd generation of PTFE, the modified PTFE. This is a PTFE that has been chemically modified with a fluorinated comonomer. The modifier perfluorpropylvinylether (PPVE) is additionally integrated into the linear chain in relation to the polymer. Though the percentage is very low (less than one percent by weight), modified PTFE has significant advantages than Standard PTFE, including:

- better weldability
- reduced plastic deformation under load
- a denser, low-porosity polymer structure
- lower permeability
- improved resilience especially at higher temperatures
- greater transparency
- improved film quality
- smoother surface.[11]

Aim of the work

The aim of this work is to study the influence of changing chemical and physical properties of Standard PTFE, modified PTFE and PTFE compounds with scientific methods to discuss correlations between their different properties and processing technologies and to discuss the new profiles for advanced applications.

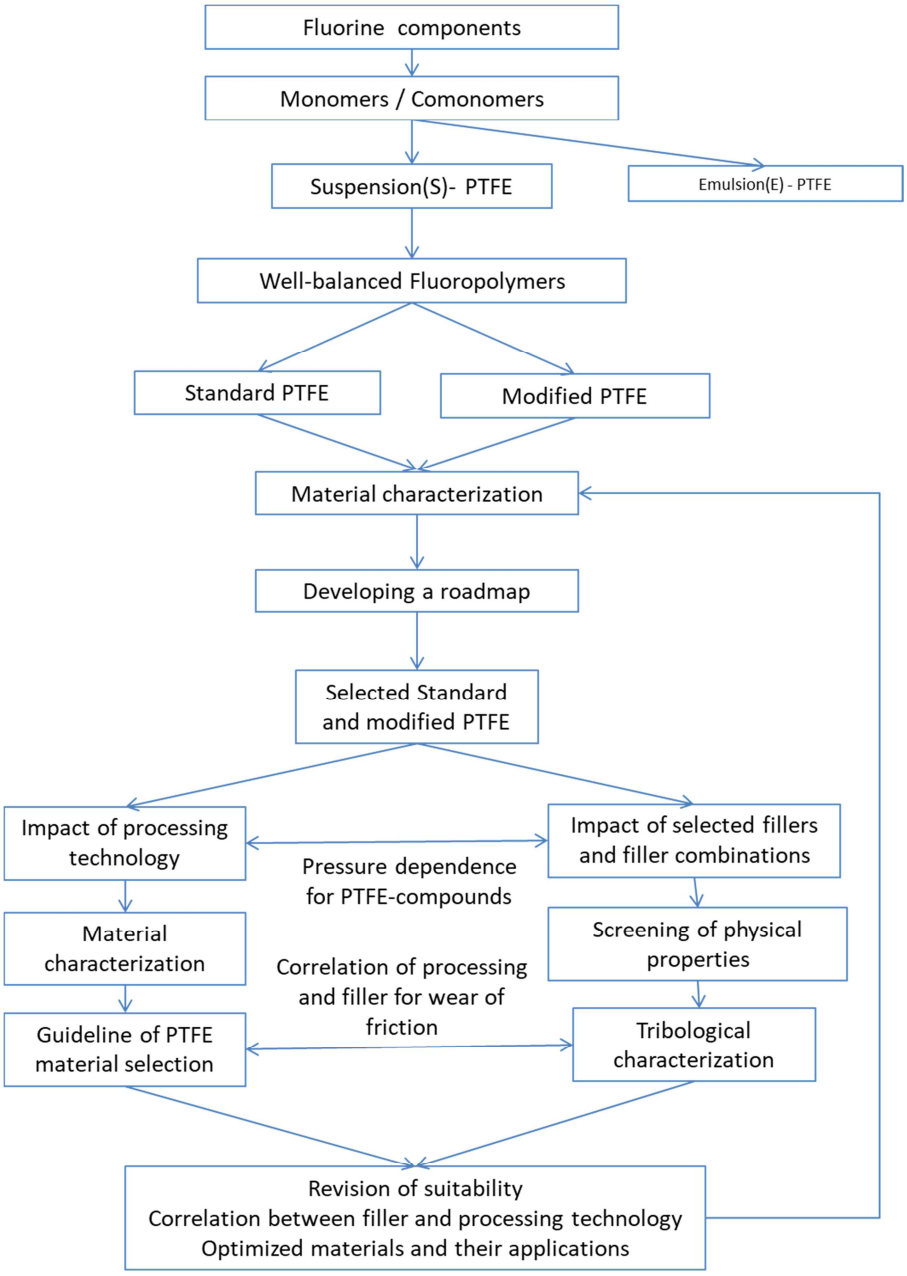


Figure 1-4: Overview of the systematic approach for optimization

Systematical approach of material selection – scientific scheme how to use

In figure 1-4 the systematic approach for material selection is demonstrated. By using systematic, application-derived material criterias, in every gate review non-appropiate material candidates are eliminated. Therefore it is not required to run through every step of this scheme with all candidates. Priorisation is made at different stages, to condense the broad variety of material candidates to finally end with the high potentials. Only these are run to the end of the systematic material selection process. These high potentials have to proof its performance in application oriented tests.

Out of the well-balanced fluoropolymers, which means to find the best compromise between low molecular weight benefits and the effect of the perfluorinated modifier PPVE, the best

candidates are selected. Therefore the major focus of this study is put on modified PTFE while Standard PTFE grades are used as references mainly.

Key benefits for selecting Standard PTFE:

- lower shrinkage than modified PTFE, therefore advantageous in processing technology
- excellent mechanical properties

Key benefits for selecting modified PTFE:

- better load and P/V-results
- stabilization effect against cold flow because of the better distribution of the crystallites within the amorphous regions
- lower wear rates especially for modified PTFE compounds due to the improved incorporation of the filler particles
- excellent mechanical properties

The correlation between the impact on processing technology and the impact on selected fillers and filler combinations is the dependence of moulding pressure. For the incorporation of fillers their concentration by weight and volume is the determining factor for the filler impact on material properties.

The kind of manufacturing technology, such as compression moulding, isostatic moulding or ram extrusion influences both, the capability to produce specific parts and the suitability to perform in the targeted application. The various manufacturing technologies, which will be described in detail later in chapter 6, are closely connected to max. achieveable part dimensions, while the sintering cycle determines the ratio of crystalline and amorphous content and thus determines properties like cold flow, permeation or flex-fatigue properties.

The main purpose of tribological characterization is the determination of the coefficient of friction and the wear. Coefficient of friction as well as wear and abrasion are mainly determined by the fillers and filler combinations. While Standard PTFE and modified PTFE are showing pretty much the same behaviour in tribological tests, the amorphous content of the fluoropolymer matrix significantly influences tribological properties.

At first in order to investigate the influences of molecular weight, molecular weight distribution and modifier content systematically a total of 15 different grades, with individually balanced modifier contents and molecular weights were analyzed due to their properties under comparable conditions. Up to now this kind of material characterization only has been applied for the differentiation between material groups, such as the PTFE and the perfluoralkoxy-polymers (PFAs). For the first time, the group of the PTFE itself is analyzed and influenced in a systematic way in order to identify the impact of molecular weight and modifier content onto the material properties for new modifications. As a consequence of this work the clearly described finger print allows, due to its specific property profile, to perform a systematic selection of materials. All materials are moulded and sintered under the same

conditions and the same kind of test specimens according to the existing standards are used. Molecular weight and modifier content are the major factors to influence the processing behaviour and material properties of the PTFE. If the molecular weight is reduced, melt viscosity decreases and particle fusion during sintering is improved. Unfortunately, low molecular weight also enhances the degree of crystallinity of the PTFE polymer thus leading to reduced physical properties. Efficient disturbance of crystallization process of a low molecular weight PTFE is required also by a perfluorinated modifier to enhance its amorphous region. As physical strength of PTFE is linked to its amorphous content, the incorporation of a side group containing comonomer guaranties for good physical properties of lower molecular weight candidates. To analyze the balancing principles between molecular weight and modifier content applied to the individual PTFE candidates is another target. An additional focus are the interphysical properties to identify the specific challenges caused by the crystalline stability of the fully fluorinated polymers.

Secondly, the physical and mechanical properties of polytetrafluoroethylene (PTFE) are influenced significantly by the processing conditions. Due to its high molecular weight, PTFE, although a thermoplastic material, is not melt-processable due to the high viscosity in the melting phase. Instead of injection moulding and extrusion, moulding by hydraulic presses and sintering are the techniques of choice to convert the PTFE from its powder state into finished parts. Both, the moulding and the sintering step play an important role for the property profile of the finished material. For Suspension-PTFE (S-PTFE) by moulding the air under the appropriate sintering conditions between the particles will mostly be removed. In case of agglomerated products, they are de-agglomerated und the contact between the surface of the primary particles is built up. Different powder properties of PTFE, such as low flow and free flow, significantly influence the required processing conditions. Final particle fusion at the outer circumference of the primary particles is the task of the sintering step. The crystalline-amorphous structure, and consequently also the property profile, is decisively determined by the cooling speed when passing the temperature of recrystallization of PTFE. The molecular structure, weight, content and distribution correlate with the physical properties so that the structure properties are cleary analyzed and interpreted.

The third part of this work deals with the impact of different fillers and its combinations to create advantageous multifunctional compounds for different applications. These compounds are selected based on their physical properties and after that a tribological characterization is made.

With all of these three sections a revision of suitability is made to have at the end optimized materials related to the specific needs of the applications. This procedure provides a way how to systematically optimize the material combination in advance. Even if the chemical structures are similar to S-PTFE, the E-PTFE products and their manufacturing processes have to be considered separately. This work only discusses material process by moulding and sintering. Furthermore PTFE compounds are typically for S-PTFE, rarely for E-PTFE, because a homogenious mixture using the E-PTFE with an average particle size of 300-600 µm is not possible.

Moreover the influences of molecular weight of the homopolymer PTFE is observed as well as the correlation of the comonomer with molecular weight in modified homopolymer PTFE.

2 Fluorine systems

This chapter deals with the base discussion on fluorine systems. The group of fluoropolymers, as well as fluor containing refrigerants, foaming agents and fire extinguishing chemicals are competing on the availibility on the highly reactice element fluorine based on the natural limited ressource fluorspar. [12] In the industry as well as in the people´s daily life all these components are very well established and difficult to replace.

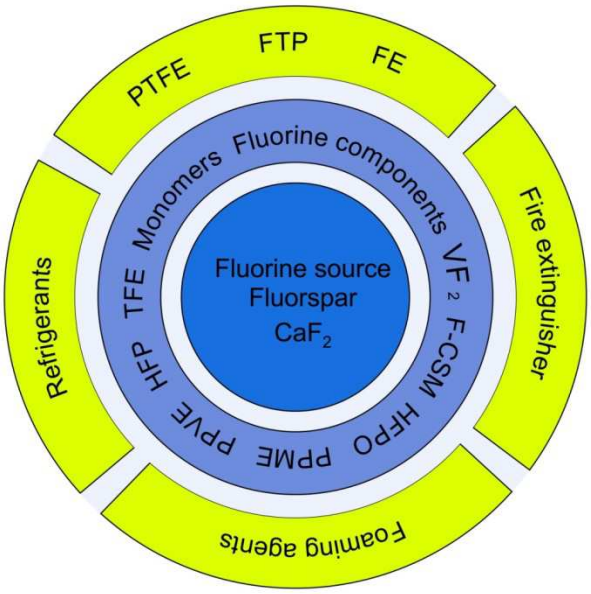


Figure 2-1: Fluorine components [24]

Beside the fluoropolymers, especially PTFE, that will be described in detail in this study, the other named fluorine components are not further observed in this work. As a short summary:

Refrigerants: In refrigerants and air conditioning, fully halogenathed methanes and ethanes have widely been used as refrigerants. [29] In 1930 Middley and Henne discovered that dichlordifluormethan can be used excellently for refrigerants in compression refrigerating machine. Hereupon a lot of methan und aethanderivate were analyzed, and much of them were convenient. Their properties fully correspond the receiveables. [15]

Foaming agents: Fluorine foaming agents such as R-225 are foaming agents which are used, e.g. for the production of personal safety goods and insulation materials for buildings. [16]

Fire exstinguisher: The function of fluorine fire extinguisher are based on surface active components. They are, among other things, contained in waterfilmbuilded foaming agent (AFFF bzw. AFFF-AR- Arqueous Film Forming Foam e.g. alcohol resistant or in FFFP – filmbuilded fluor protein foaming agents). [17]

2.1 Fluoropolymers

The todays world demand of the variety fluoropolymers is about 276.000t to estimate. The biggest amount has PTFE with 65 – 70%. As already mentioned in the introduction, fluoropolymers are a group of high performance plastics with superior properties due to the high bonding strength to element fluorine and carbon. In general the higher the fluor content, the better is the temperature and chemical resistance, the weatherability and other properties. The base for all fluoropolymers with regard to the fluorine element is the mineral fluorspar which at the moment provides sufficient availability, but basically is a limited ressource.

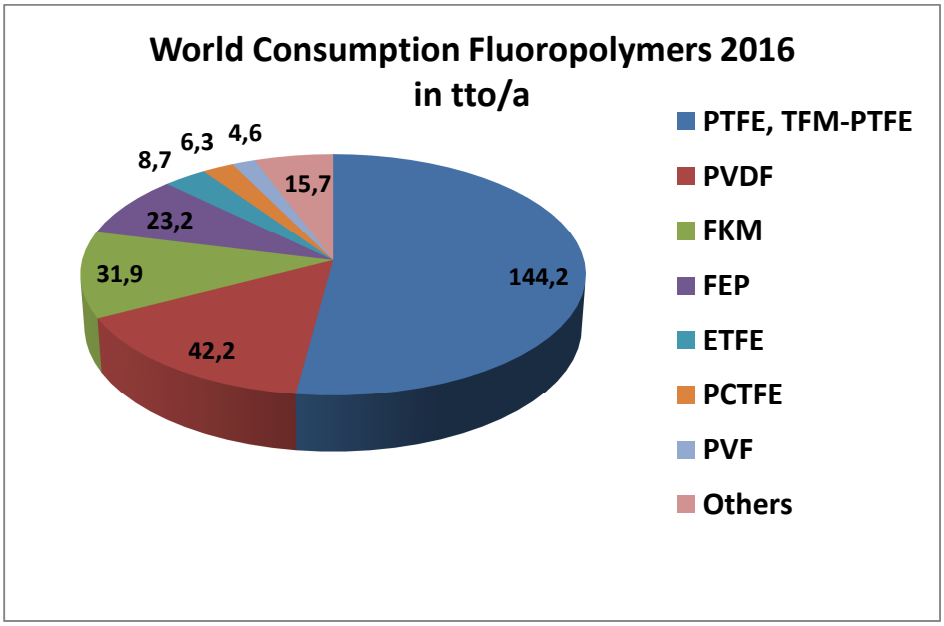


Figure 2-2: World consumption fluoropolymers 2016 [24]

In all applications, like chemical facilities, automotive and manufacturing, PTFE outperformes other non-fluorinated polymer materials as it can be seen in using the example Nylon 6 versus PTFE (Fig. 2-3). [13]

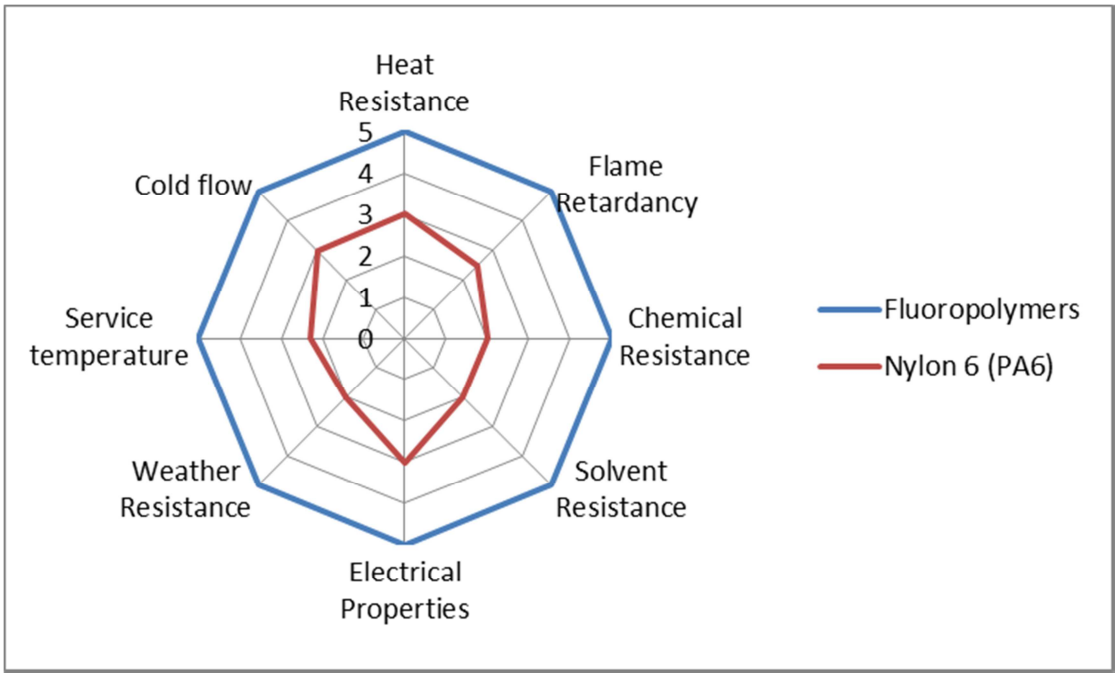


Figure 2-3: Properties of PTFE in comparison to Nylon 6 (PA6) [14]

The comparison of properties of PTFE and Nylon 6 show, that PTFE in general has improved properties compared to Nylon 6: regarding heat resistance, flame retardancy, chemical resistance, solvent resistance, electrical properties, weather resistance and service temperature. Only for cold flow, Nylon 6 with its reduced tendency, is the better material.

3 Monomers

Polymers consist of macromolecules, this means they are built up by repeating units, the so called monomers. [1] Fluoropolymers, long chain-like linear molecules, are produced by polymerization of TFE, converting chemical Pi bonds into highly stable Sigma bonds.

PTFE is formally the fluorine analogon to polyethylene (PE), which means that the C-H-bonds of the PE are replaced by C-F-bonds for PTFE. With a bonding energy of 460kJ/mol, the C-F-bond is the strongest chemical bond in organic chemistry. Because of that reason it is not possible to replace this bond by forming any other bond of higher strength. The following three factors are the reason for the nearly universal chemical resistance of PTFE: the strong chemical C-F-bond, the minimal concentration of non fluorinated end groups and the complete shielding of the stretched polymer backbone by fluorine atoms.

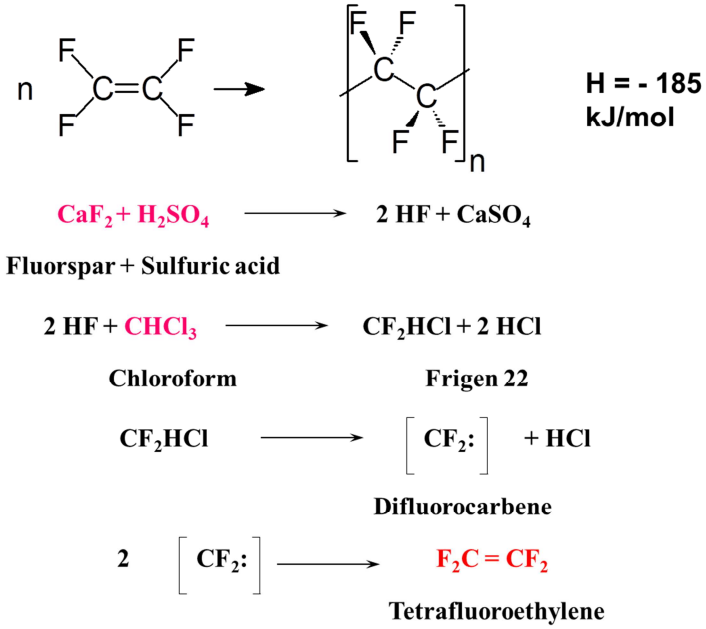


Figure 3-1: TFE Monomer Synthesis [57]

All perfluorinated polymers are based on tetrafluoroethylene ($F_2C=CF_2$), modified grades additionally contain in small quantities the comonomer perfluoropropylvinylether (PPVE). The ether-oxygen is the only atom besides carbon and fluorine incorporated in the macromolecules. The perfect shielding of the surrounding fluorine atoms ensure, that this oxygen atom does not act as a weak spot of the polymer.
The main ingredient for the preparation of TFE is the mineral fluorspar (CaF_2). As a second source, crude oil is used which, after chemical conversion into chloroform, spents the carbon atom for forming the perfluorinated molecules.
By addition of the non-volatile sulfuric acid, H_2SO_4, the highly volatile hydrofluoric acid, HF, is removed from its corresponding salt. Through exchange of two chlorine atoms in chloroform by fluorine, difluoro-chloro-methane is formed. At the market this chemical

intermediate is available under the trade mark of Frigen® 22. Treatment of Frigen® 22 at high temperature yields in the monomer tetrafluoroethylene via the di-radical difluorocarbene. The pyrolisis reaction is the dependent factor for the overall yield of PTFE production. At short contact times, low conversion and subatmospheric pressure in the tempaterature range of 590 – 900°C the pyrolisis reaction proceeds to yield better that 90% TFE. If superheated steam is present during the pyrolisis, similar results to subatmospheric pyrolysis can be achieved. Futhermore the molar ratio of steam to $CHClF_2$ is in the range of 7:1 to10:1. The pyrolysis products are cooled, scrubbed and dried. To recover the unreacted $CHClF_2$ and produce high purity TFE the resultant gas is compressed and distilled. [18]

Linear chains without branching is characteristic for PTFE macromolecules. A molecular weight determination using standard methods is not possible because of its chemical structure and high molecular weight, which makes it non soluble in all common solvents (two exceptions: PTFE has limited solubility in CFCs at elevated temperatures and in supercritical carbon dioxide). PTFE fluoropolymers are the material with the highest molecular weight in the group of thermoplastics based on linear molecules. Altough PTFE is a member of the group of thermoplastics, due to its high molecular weight, it is not processable by standard thermoplastic methods. With density measurement the relative molecular weight is determined. The density increases with higher crystallization degree and the crystallization degree decreases with increasing molecular weight. So high molecular weight PTFEs have a lower density than low molecular weight ones. Examples can be seen in table 7-3.

The main monomer of PTFE, as stated above, is tetrafluoroethylene. It is comprised of a double bonded two carbon backbone and four fluorine molecules. It is the most electronegative of all elements, has unshared electron pairs, and is more easily converted to F^- than H is to H. Bond strength is higher for C-F bonds over C-H bonds (116 kcal/mol vs. 99.5 kcal/mol). F is larger than H, and the C-F bond is more highly polarized than a C-H bond in hydrocarbons. [6]

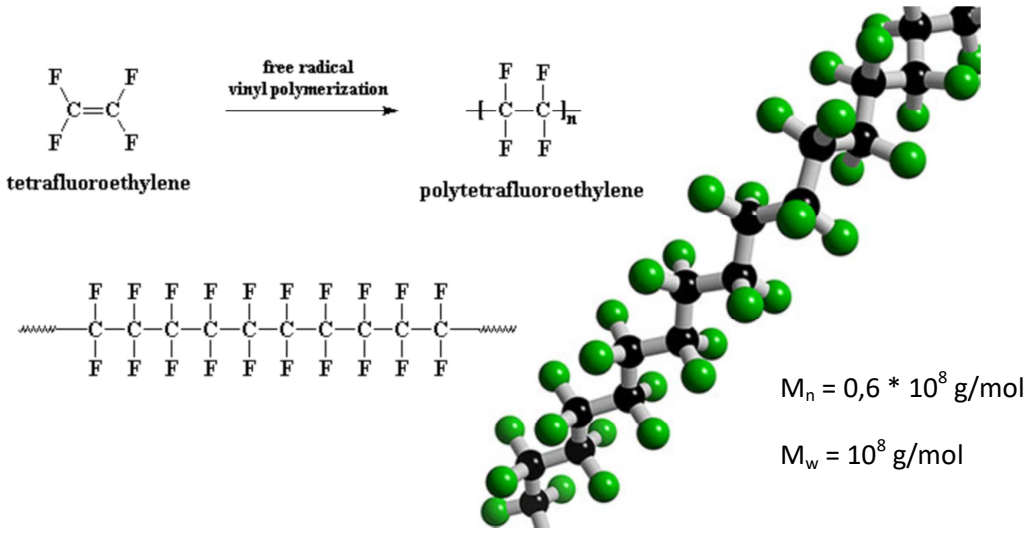


Figure 3-2: PTFE structure [6]

PTFE does not branch due to the polarity and strength of the C-F bonds. It does form a helical conformation which helps to minimize the steric repulsion of the large fluorine atoms. At temperatures of up to 19°C the polymer rotates 180° in the length of 13 carbons. Above 19°C it rotates 180° within 15 carbons length.

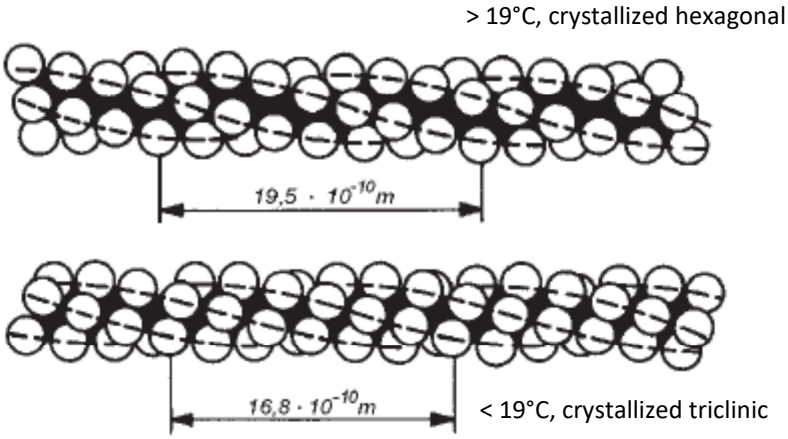


Figure 3-3: Model of molecule chain and rotation [18]

PTFE is inert to chemicals and solvents up to 300°C. In fact, the only chemicals that react with it are molten and dissolved alkali metals, chlorine trifluoride and gaseous fluorine.

Unsintered PTFE has an initial melting point of 342 (+/-10) °C and a secondary melting point of 327 (+/- 10) °C. PTFE also can temporarily withstand temperatures of 260 °C and still have the same chemical properties. PTFE retains its chemical properties in cryogenic temperatures of -250 °C. It is very stable within the full temperature range from -250°C up to +260°C. Fully fluorinated polymers are not flammable in atmospheric environment. To get PTFE to burn on its own it has to be exposed to an atmosphere of over 95% oxygen. PTFE has the lowest coefficient of friction of any polymer. [6]

4 Influence of polymerization on quality of finished products

4.1 Polymerization

For polytetrafluoroethylene (PTFE) tetrafluoroethylene (TFE) is the monomer. This monomer TFE is polymerized in water in the presence of three major components: an initiator, a surfactant in case of emulsion polymerization and other additives. For the production of the different types of PTFE two schemes of polymerization are common. The polymerzation of the monomers TFE and optionally a comonomer will be executed in water with or without additional emulsifier. If polymerized without any emulsifier it is a so called Suspension polymerization (S-PTFE), otherwise in the presence of an emulsifier it is an Emulsion polymerization (E-PTFE). [7] To realize the high molecular weight being necessary for good physical properties of fluoropolymers, all components of the polymerization reaction have to be of highest purity. Even the presence of traces of oxygen would seriously alter the polymerization mechanism. Therefore stringent absence of this „di-radical“ is a must. [18]

Suspension polymerization of TFE either can be performed in total absence of any surface active chemicals or in the presence of a very small amount of dispersant. Mild agitation of the reaction mixture and a waxy substance for absorbing coagulated seed particles set the Emulsion polymerization apart from the suspension method, demanding rigorous stirring during polymerization.

In all cases the exact polymerization technologies being practiced by resin manufacturers have to be closely monitored as these are the fundament for the different performance profile of the PTFE. The individual suppliers have its own strategy when considering the following main aspects:

- Polymerization inert gased environment (nitrogen)
- Presence of DI water
- Constant TFE pressure (typical values 8 – 20 bar)
- Isothermal or following specific temperature profile
- All chemicals used in p.a. (pro analysis) quality

This means Suspension and Emulsion polymerization differ in a number of ways but the most important are the amount of surfactant added to the polymerization reactor and the shear rate applied a specific stir system during the reaction. For the Emulsion polymerization much more surfacant is needed than for the Suspension process as it produces small submicron particles in the range of 250 nm which are the basis for “fine powder” and “aqueous dispersion” products. The suspension process generates long tough particles in the size of 1 – 15 mm, which are cut and screened in a finishing step to produce “granular” resins. S-PTFE has a high molecular weight and is usually converted into finished products by moulding and sintering by an alteration of sintering ceramics called compression moulding. For this compression moulding a „preform“ is made by compressing it in a form. After that the preform is sintered in an oven, which means melted and densified into the final shape. There

also exist some other moulding techniques which are also described in the next chapter. E-PTFE is processed by forming a paste by the addition of an isoparaffin lubricant. This paste is then extruded into tubing, wire insulation, tape or membrane. Typically, the extruded shape is dried in an oven and the lubricant is removed. In the final step, the dried extrudate is sintered in an oven. As a subgroup of Emulsion PTFE aqueous dispersions are being manufactured. These dispersion products are formulated into coatings by the addition of resins, pigments, and other additives. [18]

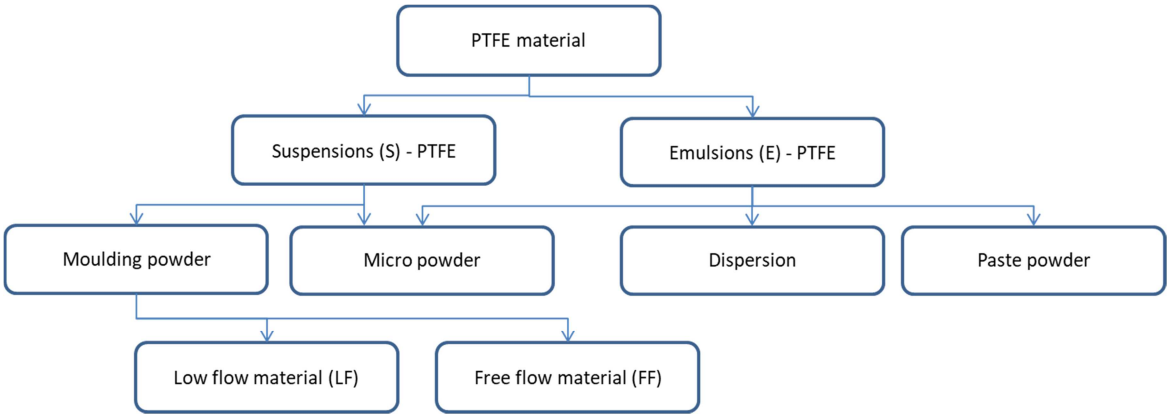


Figure 4-1: Overview PTFE material [7]

4.2 Polymerization mechanism

The polymerization of PTFE is acted by a free radical mechanism and this reaction is initiated by a catalyst or by an initiator at different temperatures. For higher temperatures TFE polymerization can be initiated by persulfate while at lower temperatures a co-initiator such as bisulfite is required.

By enhancing the molecular weight of the polymer the extent of crystalline region formed during recrystallization is reduced. The exceedingly long chains of PTFE have a much better probability of chain entanglement in the molten phase and no chance to crystallize to the premelt extent (>90–98%). This is exactly the reason that it is essential to polymerize TFE to a degree of polymerization of $P_N = 10^6$ for commercial applications. To control the molecular weight of PTFE special polymerization parameters are important, for example initiator content, concentration of TFE within the aqueous phase, telogens and chain transfer agent, in special cases when required to achieve a very broad molecular weight distribution. For PTFE the melt viscosity is about $10^{10\text{-}12}$ Pas at 380°C. Although PTFE develops only minor flow upon melting, it may be a thermoplastic material due to the molecular design. The closure of voids in particles made from this polymer does not happen with the completeness of the other thermoplastics such as polyolefins. A small fraction of void volume remains in parts made from homopolymers of PTFE due to the difficulty and slow rate of void closure in this polymer. Voids affect permeation and mechanical properties such as flex life and stretch-void-index. The stretch void index is an indication of the number of voids in PTFE materials,

while the flex life is defined as a number of cycles that a part can withstand before disastrous fatigue failure occurs. [53]

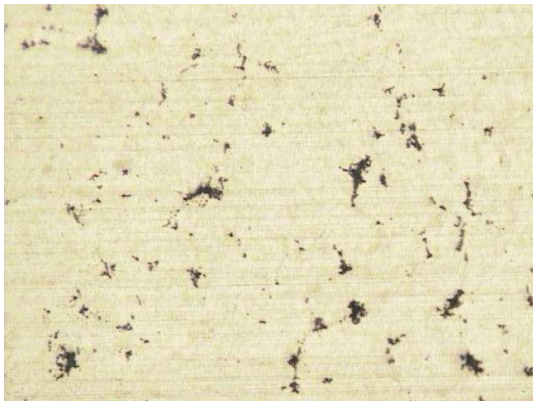


Figure 4-2: Voids in PTFE-material

Voids can act as a catalyst for crack and other material defects. To meet the demands of extreme mechanical properties and resistance to permeation, the residual voids must be eliminated. Solving this problem requires a reduction in the viscosity of PTFE without extensive recrystallization. The remedy has been to polymerize a small amount of a comonomer with tetrafluoroethylene to reduce the molecular weight and to disrupt the crystalline structure of PTFE. In this case perfluoropropylvinylether (PPVE) as a modifier is recommended. [18]

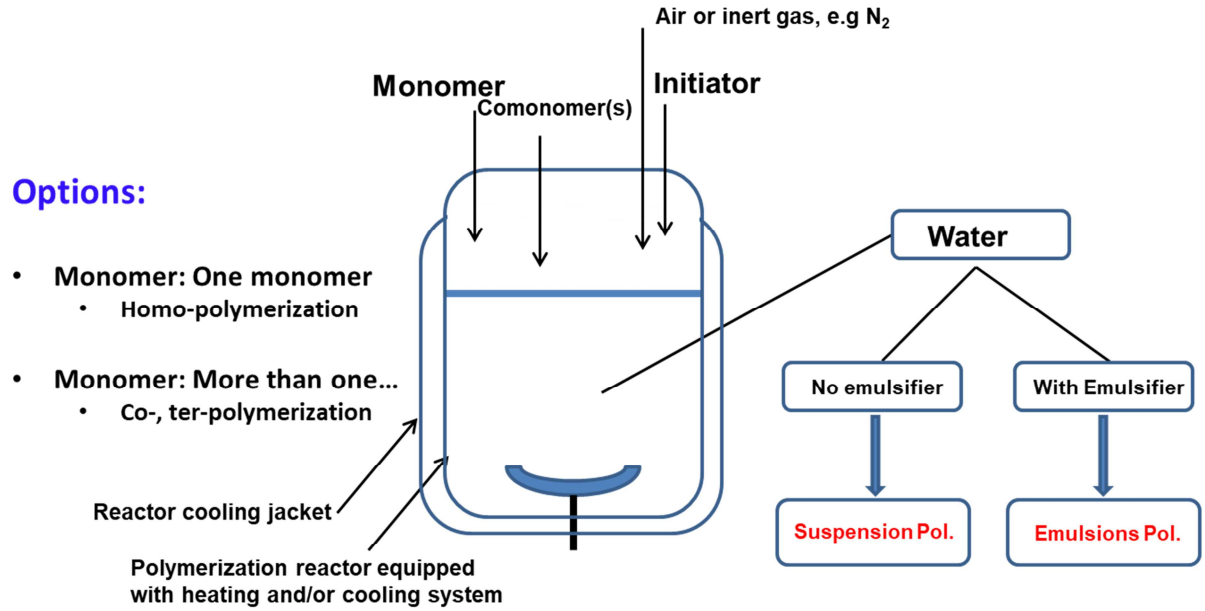


Figure 4-3: Polymerization process in Suspension and Emulsion

4.3 Suspension polymerization – properties und quality characteristics

Industrial Suspension polymerization usually proceeds via a free-radical mechanism to produce polymer beads. The size distribution of the polymer beads is often similar to that of

the polymerizing drops in the reactor. That distribution is determined by the operating mechanisms of drop breakage and of drop coalescence. Consequently, the value of the Reynolds Number is significant and a potential change in flow regime must be considered in reactor scale-up. The choice of suspending agent, which can be a watermiscible polymer or a finely divided particulate solid, can effect both, the drop size and the properties of the final product. High monomer conversions are attainable but reaction kinetics is effected by increases in drop viscosity during the polymerization. Drop mixing, which sometimes takes place, can be slow, so that non-uniformity occurs in the final product. With copolymerization, complications can arise if the initiator, or one of the monomers, is partially soluble in the continuous phase. Adverse environmental impact of Suspension polymerization can be avoided by cleaning and/or recycling of the continuous phase when it leaves the reactor. [19]

In Suspension polymerization, drops of a monomer-containing phase are dispersed in a continuous liquid phase and polymer is produced inside the drops. In many cases, the monomer contains no diluent and the chemical reactions that occur inside the drops are very similar to those that are found in bulk polymerization. In most Suspensions, polymer is formed via a chain reaction. In most industrial Suspension polymerization agitated batch (or semi-batch) reactors are used and the continuous phase is aqueous. That is advantageous because the process is often exothermic and good heat transfer from the reactor is required. The ratio of surface area to volume is relatively high for small drops so that the rate of heat transfer to the aqueous phase is high. Although drop viscosity may increase substantially, the overall viscosity of the suspension is usually much lower than that which is encountered in the equivalent bulk polymerization. Consequently, agitation of the reactor contents is possible and heat transfer via the aqueous phase to the reactor wall is good. Also, high conversions of monomer to polymer can be achieved inside the drops whereas, in bulk polymerization, increasing viscosity of the polymer monomer solution often limits the extent of monomer conversion. Suspension polymerization is particularly useful when the final polymer is required to be in the form of small beads. However, product contamination can be a problem if the drop stabilizers cannot be removed. Suspension polymerization usually requires larger reactor volumes than bulk processes because the vessels are usually filled half by water. [19]

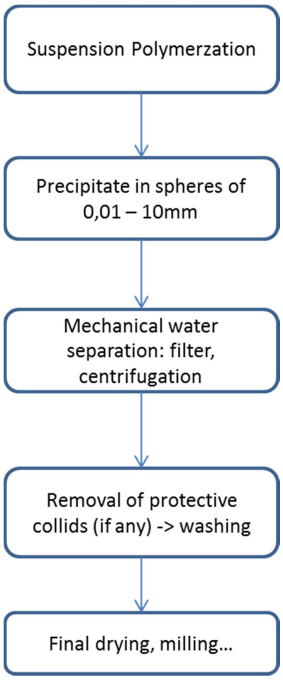


Figure 4-4: The working-up of Suspension polymer [7]

Preparation of PTFE by Suspension polymerization

To produce Suspension PTFE the PTFE commercially is polymerized in an aqueous suspension medium. An elevated temperature and pressure with only little or no dispersion agent and vigorous agitation are important characteristics of this polymerization system. Disintegrating its particles and drying to obtain a powder, which can be moulded by commercial processes, finishes the suspension recovered from the reactor. Ethylene, hexafluoropropylene and alkylvinyl ethers and their fluorinated versions are included in the commercially important comonomers. By introducing the monomer into an aqueous medium containing a polymerization initiator und pressure the polymerization is achieved. It is possible to add a dispersing agent to the aqueous phase to seed the polymerization. The PTFE polymerization is done under constant pressure conditions for controlling the molecular weight and its distribution. The pressure range is about 0.03 – 3.5 MPa and must be held constant by feeding monomer into the reactor. The initiator and temperature are interrelated. The initiator amount varies in the range of 2 – 500 ppm, based on the weight of the water. The polymerization conditions influence the exact concentration. The molecular weight is reduced, when initiator is too much, while all other variables are held constant. On the other hand low initiator ratio leads to a poor polymerization yield. For the initiator and the heat transfer medium for the exothermic heat polymerization water is the carrier. Water does not interfere with the reaction but most organic chemicals, even in low concentrations, do. [18]

At moderate pressures (0.8 – 2.0 MPa) and temperatures (15 – 80°C) TFE polymerizes easily. Controlling the rate and transfering the heat generated by the exothermic polymerization reaction is required. This can be reached by cooling the aqueous phase, which is the heat transfer media, and by circulating a cold fluid through the polymerization reactor jacket.

While suspension process it is an important concern that PTFE build up on the inner wall of the reactor. This would reduce the heat transfer. By adjusting the temperature of the coolant medium in the jacket the temperature is controlled. String shaped particles are the product of Suspension polymerization, which have variable sizes and shapes and are elongated as a result of vigorous agitation, resembling shreds of graded coconut. To convert the polymer into a usuable form two processing steps are needed. Firstly the water must be removed and the polymer should be rinsed and dried. Secondly there has to be a reduction of the particle size. This can be done before or after drying. [18]

Advantages of Suspension polymerization:

- Low viscosity due to the suspension
- Easy heat removal due to the high heat capacity of water

Disadvantages of Suspension polymerization:

- As particles obtained by suspension polymerization, typically in the range of 1 -15 mm, it cannot be used for polymers showing particles in the nano range (50 – 250 nm, typical size for Emulsion polymerization)
- Cannot be used for the manufacturing of aqueous dispersions and coagulated aqueous dispersions (fine powders) as the required primary particles range of 50 – 250 nm can not be achieved

Standard S-PTFE and modified S-PTFE are milled with the same processing technology and after that cleaned from chemicals of polymerization. The mechanical separation of the end product from water will follow up drying and fine milling. Then the material should have a particle size of about 25 µm and has a rough surface. This is why it is named „low flow“ PTFE. This material is the base product for agglomeration to „free flow“ PTFE material or for the production of compounds.

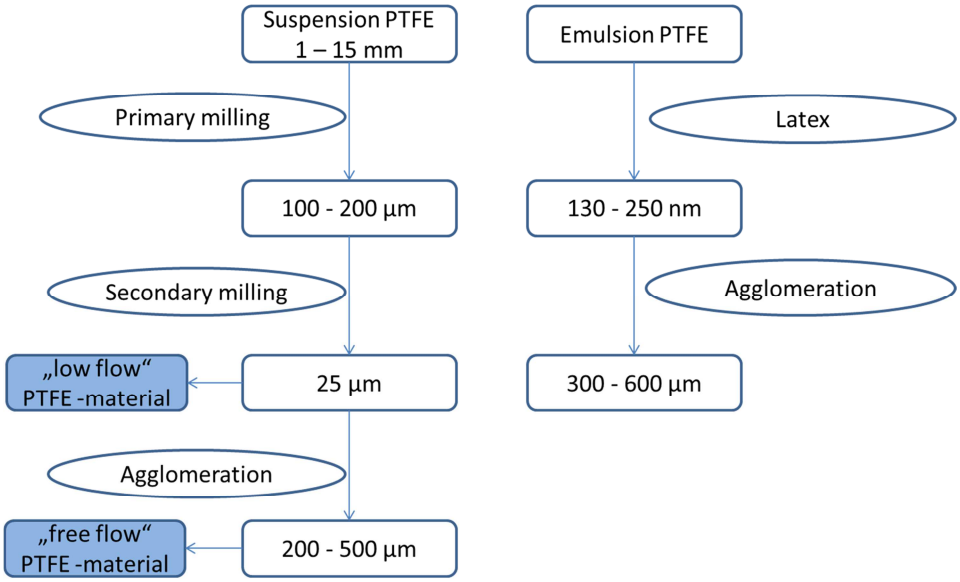


Figure 4-5: Particle sizes for S-PTFE and E-PTFE

For producing free flow PTFE the low flow material will be mixed with non mixable liquid to create agglomerate grains, which have a grain diameter of about 200 – 500 µm. They will be separated from the liquid and dried. They are called free flow because the particles are round and the surface is very smooth. With free flow material the manufacturer has the opportunity for automatical charging and fully automatical processing with a high efficiency.

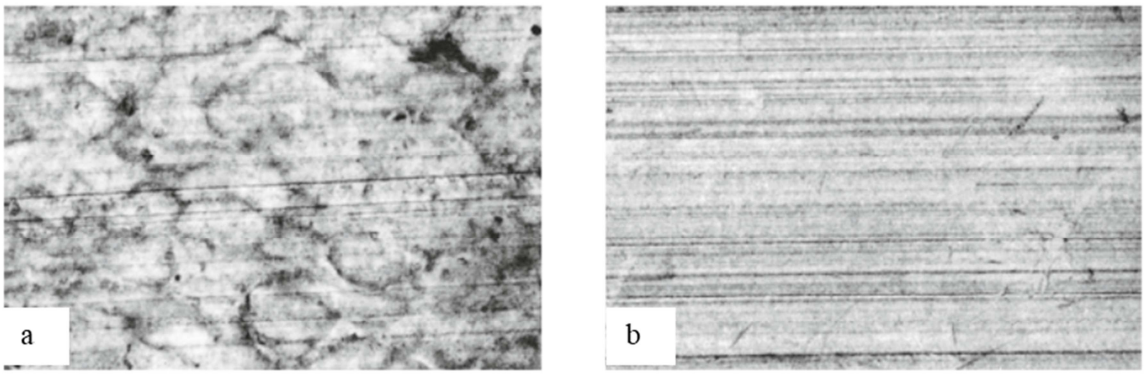


Figure 4-6: a) Standard PTFE, the original particle boundaries are clearly discernible after the sintering process, b) Modified PTFE, the original particle boundaries are no longer discernible because of better fusion between the particles

Producing compounds will be done with low flow material because due to the lower particle size the filler distribution is more homogenious. [7]

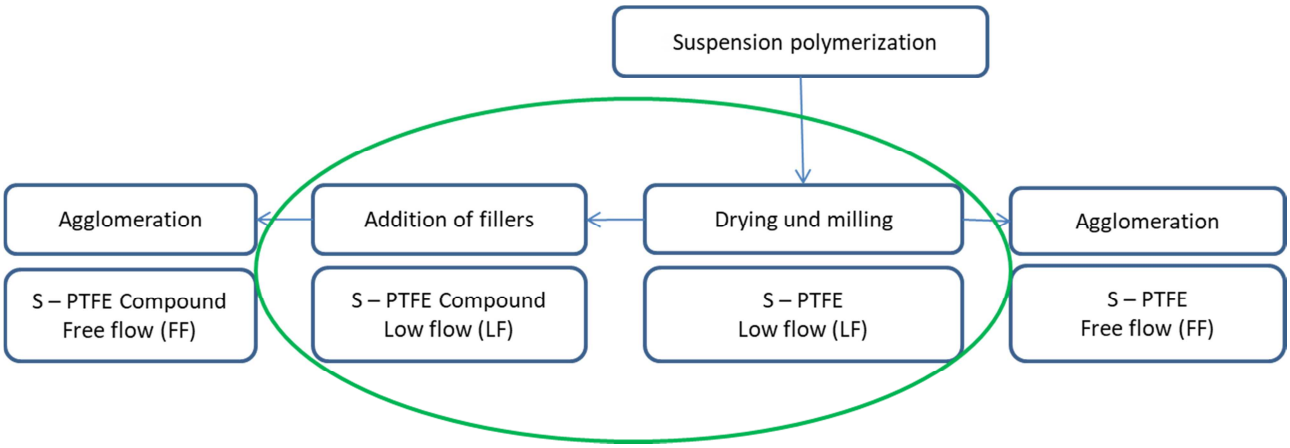


Figure 4-7: Manufacturing process for S-PTFE – green marked area is the focus of this study [7]

4.4 Emulsion PTFE - properties and quality characteristics

For the Emulsion polymerization the polymerization medium contains a fully fluorinated emulsifier, which is chemically inert under reaction conditions. In this case the PTFE primary particle size is increasing continously throughout the polymerization reaction, finally reaching at the end a size of about 250nm. [7]

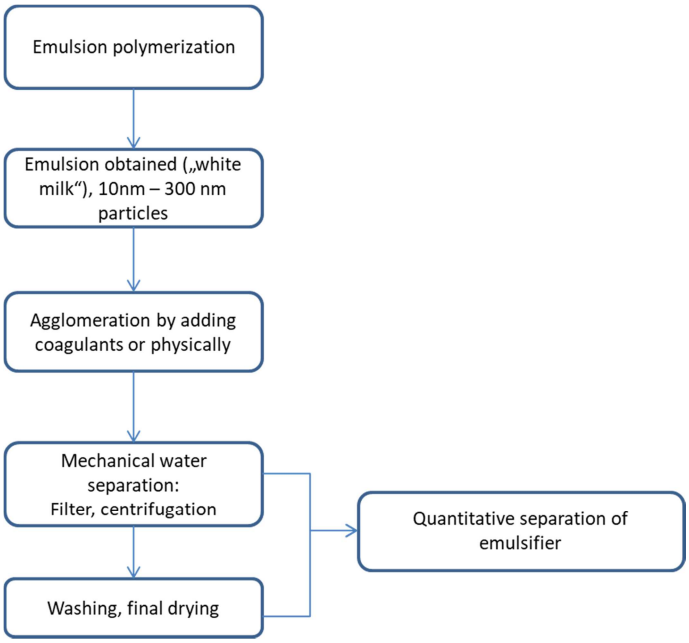


Figure 4-8: The working-up of Emulsion polymers [7]

The simultanious increase of all particles over the whole reaction time allows through regulation of the reaction conditions to build up a core-shell-structure. After ending the polymerization the polymer in form of dispersion at first is coagulated to 300 - 600µm sized agglomerates, so called secondary particles. The aqueous phase and polymer phase are mechanically separated and dried. While reprocessing the emulsifier is separated and recovered highly efficient. As a consequence the paste powder is practically free from emulsifier.

Advantages for Emulsion polymerization:

- Thermal and viscosity problems are minimized due to the high heat capacity and ease of stirring of the continuous aqueous phase [18]
- A high reaction speed enables high and economical productivity
- Polymers with bimodular molecular weight distribution are easy to be prepared by the addition of radical trapping agents towards the end of the polymerization process

Disadvantages for Emulsion polymerization:

- No fine cut grades in the range of 20-40 µm, which are the base material for compounds
- Due to the presence of the emulsifier the polymerization system is more complex and if the surface can not be removed completely during working up they may act as an impurity for PTFE

In this study only Suspension polymerization is described in detail and focussed because the properties of compounds are aimed and they base of S-PTFE. Furthermore the aim of the work is a global overview of modified PTFE and this is only possible in the field of Suspension polymerization not Emulsion polymerization.

5 Investigation of well-balanced fluoropolymers

5.1 Impact of molecular weight and molecular weight distribution

The meaning of the term „high performance polymer materials“ has changed during the last several years as a result of significant progress in polymer chemistry and the rapidly growing variety of polymer material applications. The main reason is in a large number of new applications requiring new features such as high chemical resistance, high or low heat conductivity, special surface properties, high purity and other special performance properties, combined with high temperature requirements. Moreover, in some new applications properties others than temperature stability, e.g. excellent electrical insulator combined with high thermal conductivity, may become much more important for providing high performance. The other „classical“ approach in qualifying a polymer as a high performance material was based on business practice, such as service temperature of the resin. According to this logic, all polymers that are showing higher service temperature than 150°C should in reality be considered as high performance materials. [22]

The molecular weight of a molecule is the total of the atomic weight of the atoms contained in the molecule. In the field of low molecular weight products every substance has a definite molecular weight. In difference to that, for polymer materials there is no uniform molecular weight because of the production process. The macromolecules have different length. This causes a molecular weight distribution. The width of the molecular weight distribution depends essentially on the type of polymerization. The influence of the molecular weight distribution can happen during the reaction process for example by changing the monomer concentration in reaction preparation, the initiator concentration, the temperature, the pressure, the solid content and the mechanism of termination of the polymerization process.

For the evaluation of the properties for polymers the molecular weight distribution in dependency of degree of polymerization is important. In general it is assumed, that narrow distributions of the molecular weight have higher uniformity for the specific values, a more narrow thermal softening area, less sensitivity for stress and strain and a better chemical resistance.

Broad distribution of the molecular weight has advantages in processing, because the low molecular fractions are a kind of lubricant. The brittleness of the polymer material is decreasing, as a consequence of the low molecular bonds operate between the macromolecules as softener. For semi-crystalline thermoplastics the crystallization degree is reduced, because more disruptions of the allover structure are possible. [2]

With increasing molecular weight, equivalent with increasing chain length, the entanglement of the single macromolecules also increase. Thus the movement in melting, especially the sliding to each other, is interfered. By increasing entanglements and bigger chain length the movement is interferred and the crystalline formation is hindered, so as to higher molecular

weight the crystalline amount is decreasing - simultaneously the amorphous content goes up. This goes along with the decreasing of the density, the E-modulus and the wear of friction. [2]

The molecular weight of PTFE is rather high, in the range of 1 to 5 * 10^8. Such a high value is the main reason for extremely high melt viscosity, which is increased by a factor of 10^6 above that of the most polymers and consequently too high for melt-processing methods used in the fabrication of common polymers. However, the high melt viscosity is not only a function of the high molecular weight. Molecular weight also effects the crystallization rate (decreases with increasing molecular weight) and specific gravity. The standard specific gravity (SSG) is calculated from the number-average molecular weight M_n. [23]

5.2 Influence of molecular weight distribution

A typical polymer sample contains chains with a wide distribution of chain length and some molecules of very high molecular weight. Upon the specific conditions of radical polymerization the exact width of the molecular weight distribution is up to M_w/M_n approximitely 2. As an example the polymerization of some olefins can result in molecular weight distributions that are extremely broad. M_w/M_n is a typical value and some special types, for example PTFE-MC-2, are located wide above in the range of 30 – 35. In other polymerizations, polymers with very narrow molecular weight distributions can be obtained. Many polymer properties, such as melt viscosity, are depending on molecular weight and molecular weight distribution. Therefore, it is useful to define molecular weight averages associated with a given molecular weight distribution as detailed in this section. [25] It turns out, that in case of PTFE products broad molecular weight distribution is rather beneficial for the performance profile of finished goods: the low molecular weight of the part polymer enables good powder flows during moulding while the extremely high molecular weight fraction acts as tie-molecules connecting the individual crystallites with each other.

5.3 Effect of molecular weight on polymer properties

A significant effect on the mechanical and physical bulk properties on polymers can be postulated extinguished by molecular weight and dispersity. With a higher molecular weight in general it can be said, that it improves the mechanical properties so that elongation at break and tensile strength increase. Furthermore the melt and glass transition temperatures are functions of the chain mobility, within the crystallites and the amorphous regions. Due to the extremely high melt viscosity of the PTFE, processing and forming of the polymeric material will be more difficult.

An opposite effect has the dispersity. A lower dispersity (narrow distribution) leads to better mechanical properties, while a broad molecular weight distribution lowers the tensile properties in general but increases the yield strength and the film-forming behaviour in

coatings. The high molecular weight portion may cause processing difficulties because of its significant contribution to the melt viscosity, while the low molecular weight portion of the distribution has a similar effect as a plasticizer, which reduces the brittleness and lowers the melt viscosity to improve the processability. [25]

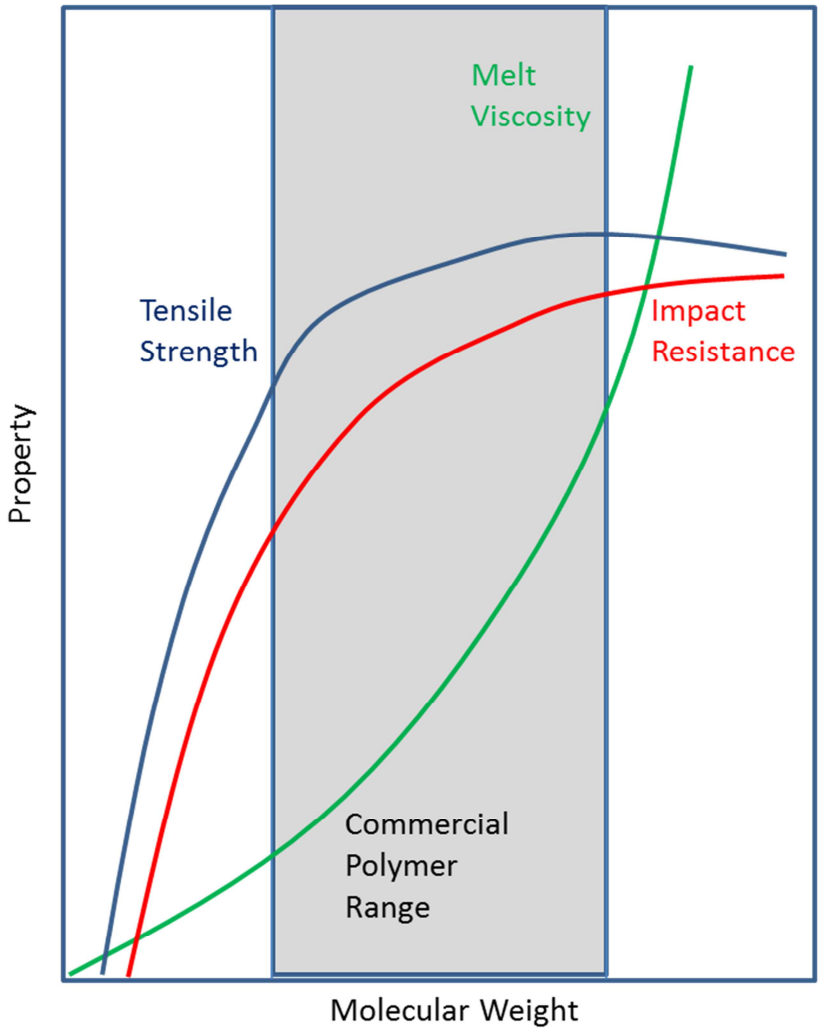


Figure 5-1: Molecular weight and properties of fluoropolymers [51]

As can be seen in figure 5-1, tensile strength and impact resistance show an overproportional increase as the molecular weight gets higher. For fluoropolymers it can be said, that after reaching the specific molecular weight no further provement of mechanical properties is possible. The commercial polymer range is marked in grey.

5.4 Impact of modifier content

Manufacturing of modified PTFE

The copolymerization is performed in an aqueous Suspension polymerization under practically the same reaction conditions as the homopolymerization of TFE at pressures from

0.6 to 1.2 MPa and in a temperature range of 15 – 80 °C, with constant pressure over the polymerization time.

The same initiators as for homopolymerization are used, preferrably ammoniumpersulfate or alkalipersulfate in combination with bisulfite co-initiator in particular for lower polymerization temperatures. Mainly the polymerization is done in the presence of buffers like NH_3, $(NH_4)\,CO_3$ and ammonium or alkali oxalates. As an option minute amounts of a perfluorinated emulsifier reduces the size of the crystallites within the polymer particles significantly. The resulting improved deformability of the moulding powder is the origin of its better performance profile. As requested by the copolymerization kinetics, the comonomer is fed into the reaction vessel before the start of the polymerization or partially before the start and continously during the polymerization. [54]

According to conventional copolymerization kinetics over the polymerization time the TFE pressure is kept constant and PPVE (perpropylvinylether) is replenished to enable its statistically distributed incorporation into the molecular chain.

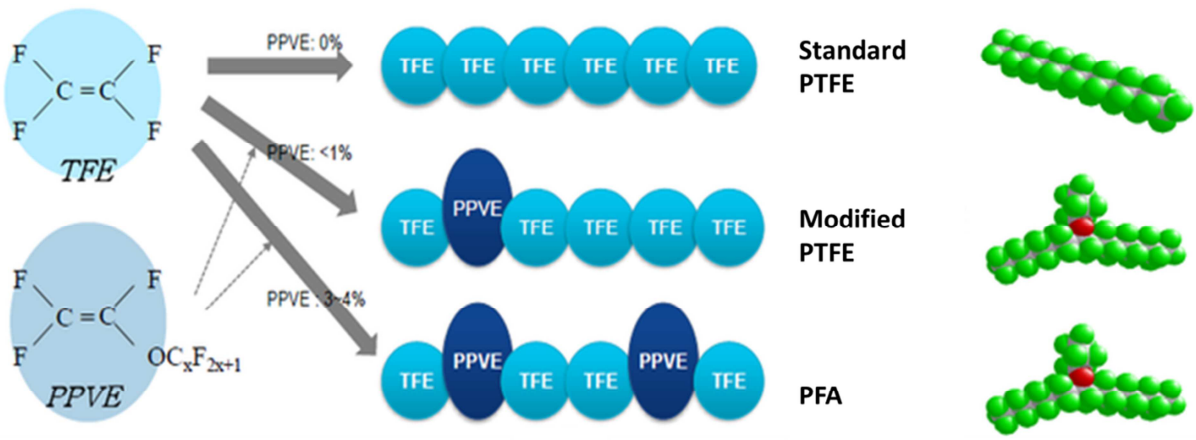


Figure 5-2: PPVE content [60]

To determine the PPVE content IR-spectroscopy is used by comparing the absorbance at 995 cm^{-1} for PPVE, 1090 cm^{-1} for perfluoroethylvinylether (PEVE) and at 889 cm^{-1} for perfluoromethylether (PMVE), respectively with the absorbance at 2365 cm^{-1}.

The reduction of deformation under load, the so-called cold flow, which is enabled by the crystalline regions of the polymer, is signifacantly reduced by the incorporating minute amounts of PPVE into the PTFE molecular chain. PPVE prove to be a proper comonomer due to its excellent thermal stability at processing temperatures and chemical stability in the finished product. In small amounts of 0.01 – 0.1 wt% PPVE is sufficient to reduce the crystallinity of PTFE and thus improving physical properties. [26]

Control of the molecular weight

If the comonomer decreases during the reaction, the polymerization rate increases and consequently the molecular weight. To keep the molecular weight under control, a constant ratio has to be accurately maintained over the polymerization time. Another consequence is the inevitable decrease of the molecular weight by the increase of the comonomer content.

The work-up of modified PTFE is the same as with Standard PTFE. The Suspension polymerisate is carefully washed, dried and grinded to a particle size of 10-50 µm for low flow moulding powders or granulated by the addition of organic solvents for free flow moulding powders. Chemicals from the polymerization have to be carefully removed to avoid brownish or grayish discolouration at the processing stage. Decarboxylation of the end groups may occur at the practiced drying temperatures that are above 180°C. [26]

5.4.1 Characterization of modified PTFE

The comonomer and amorphous content quantities are conveniently measured via IR spectroscopy. The determination of the comonomer content is sensitive down to 0.005 mol%. Figure 5-3 below gives a detailled view on the FT-IR spectroscopy. For the IR-spectrum two different areas exist: above 1500 cm^{-1} the absorption bands can be found, where the functional groups is related, while in the area below 1500 cm^{-1} bands can be contained und the molecule is characterized in whole. Therefore this area is also called the „finger print area“. [31]

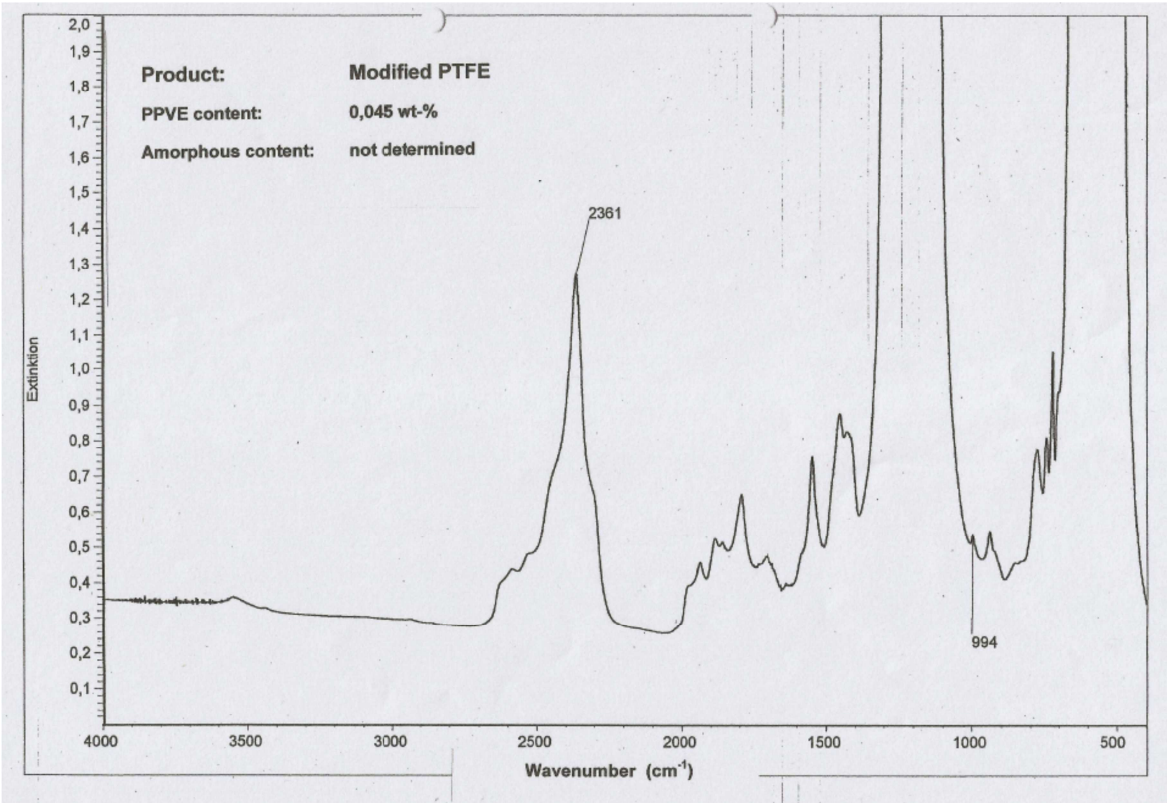


Figure 5-3: FT-IR spectroscopy for PTFE (the absorbance at 994 cm^{-1} and at 2361 cm^{-1}) [31]

For the absolute determination of the molecular weight of high molecular weight PTFE there is still no reliable method available because of its insolubility in organic solvents below its melting point. Above the melting point dissolution occurs in perfluorinated solvents but is prone to chain degradation. By the heat of crystallization or the standard specific gravity (SSG) normally the molecular weight is estimated indirectly. Founded are both methods in the increasing amorphous content with increasing molecular weight. Most SSG methods depend on the void content which can be significantly influenced by the reaction conditions. As an example the lower the polymerization temperature and the higher the TFE pressure, the better is the deformability of the finely ground powder, and consequently the lower the void content. This method can not be applied for modified PTFE because since the copolymerized PPVE alters profoundly the crystallization and deformability. In uniformity the factor 2 arises from termination by combination. The copolymerization of PPVE is accompanied by a transfer reaction which results in a decrease of the molecular weight. About the side reaction little is known but it is favoured by higher comonomer concentration, lower TFE pressures and higher polymerization temperatures. With iso-perfluoropropyl vinylether the transfer reaction is significantly accelerated. As a consequence the used PPVE has to be essentially free from this isomer. [26]

5.4.2 The influence of the PPVE content on the physical properties

With the decrease of the molecular weight at least by a factor 2 a highest comonomer content is expected, whereas the SSG and degree of crystallinty seems to be basically unchanged. This might be randomly since the crystallinity decreasing with higher comonomer content may be compensated by the simultaneous decrease of the molecular weight. The best demonstration for the influence of even minute comonomer contents, in this work between 0.03 and 0.11 wt%, on the crystallization behaviour is the comparison with Standard PTFE. At the same degree of crystallinity, the smaller crystallite size results in more tie-molecules bridging the adjacent lamellae, because with small crystallites the requirements to tie-molecules, being incorporated in more than one crystallite, is easier to be fullfilled. Furthermore lower molecular weights can contribute to the tie-chain concentration. This phenomenon is reflected in low strain properties such as modulus and cold flow.

Another typical characteristic for modified PTFE is the intrinsic decrease of the melt viscosity. The incorporation of the comonomer PPVE is resulting on the tendency of slightly increasing melt viscosity despite a decrease of the molecular weight by a factor of 2. The melt viscosity for linear polymers is proportional, therefore it should decrease by a factor of 10. The observed increase is due to the bulky side group of the polymer chains. The disentangling of the polymer chains thus appears to be drastically hindered. This phenomenon shows up with large strain properties such as ultimate tensile strength and elongation at break. As commercial grades of modified PTFE consist of polymers with decreased molecular weight by factor 3 – 5, the observed melt viscosity is slightly reduced, well known from the increased tendency of sagging when sintering large billets.

Modified PTFE has an excellent weldability due to its lower melt viscosity. The quantitative determination of the weld factor is performed by analyzing the stress-strain behaviour of original and welded specimens (Fig. 5-4).

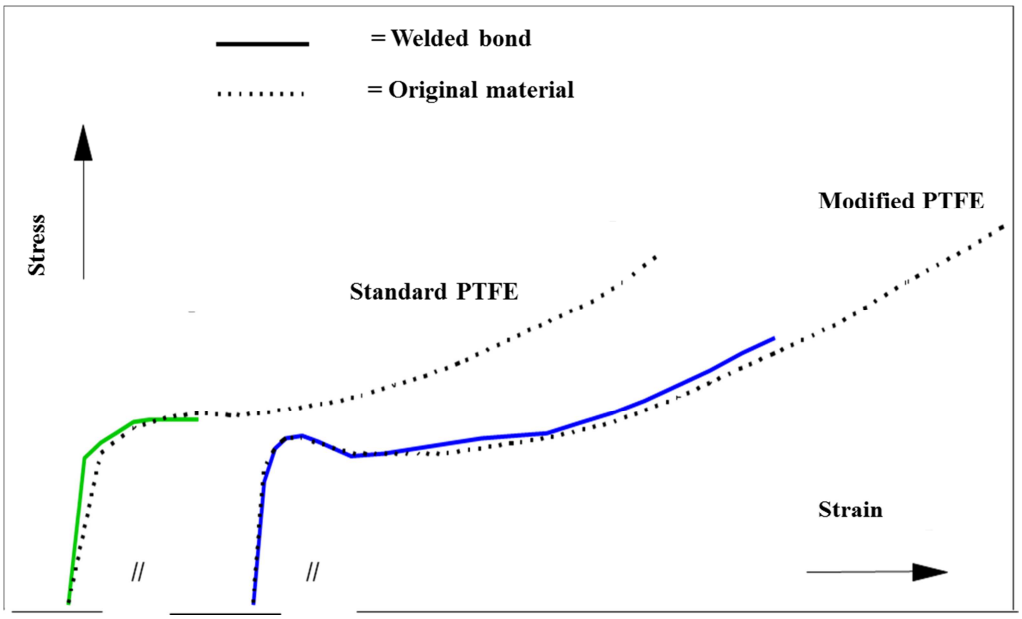


Figure 5-4: Strain-stress-curves for Standard and modified PTFE for original material and welded bond [58]

The difference becomes clearly visible when comparing modfied PTFE with conventional Standard PTFE. The possiblity to weld is an important benefit for modified PTFE and the weld strength seems to be beneficially influenced by the altered crystallization behaviour, leading to more physical crosslinkings which prevent the polymer chains being pulled out of the interphase during cooling. [26]

6 Observation of Standard PTFE and modified PTFE

6.1 PTFE - a semi-crystalline material

There is a special characertistic for thermoplastics. If the polymers can move freely, coils will be build up. When the macromulecules are absolutely linear and completely regular, then these polymers built crystalline and amorphous regions, when the movement of the molecules is decreasing during cooling. The composition of the crystalline-amorphous material is defined by the Gibbs Helmholtz equation $\Delta G = \Delta H - t*\Delta S$; the minimum of G defines the composition of lowest energy.

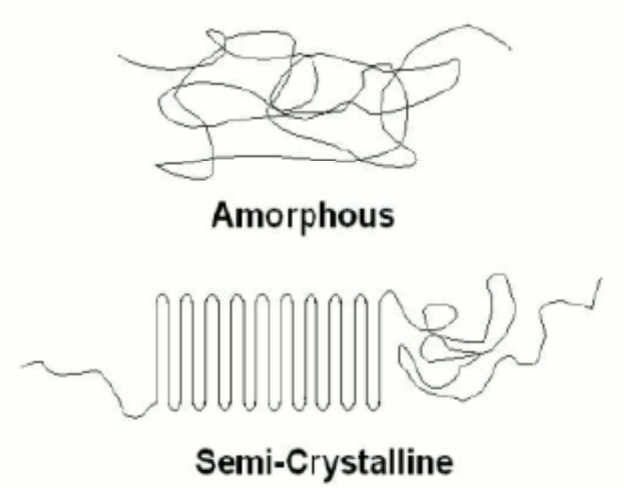


Figure 6-1: Amorphous vs. semi-crystalline [27]

In general superlattices are known for thermoplastics, but in difference to the conventional thermoplastics PTFE has no spherolithes because of its high viscosity. The lamellar crystallization structures are regionally distributed so that the formation of superlattice is not possible.

Those polymers are called semi-crystalline, because a fully crystallization is practically not possible. After the main part is folded into crystallites, also residual molecular parts are left in unordered structure. These thermoplastics exist of semi-crystalline structures, which are embedded in amorphous regions. In a lot of respects this crystalline condition give these polymers a special character. Essentially it is the higher stiffness to thermal distortion, which is defined by the crystalline regions, while toughness is part of the amorphous sections. [1]

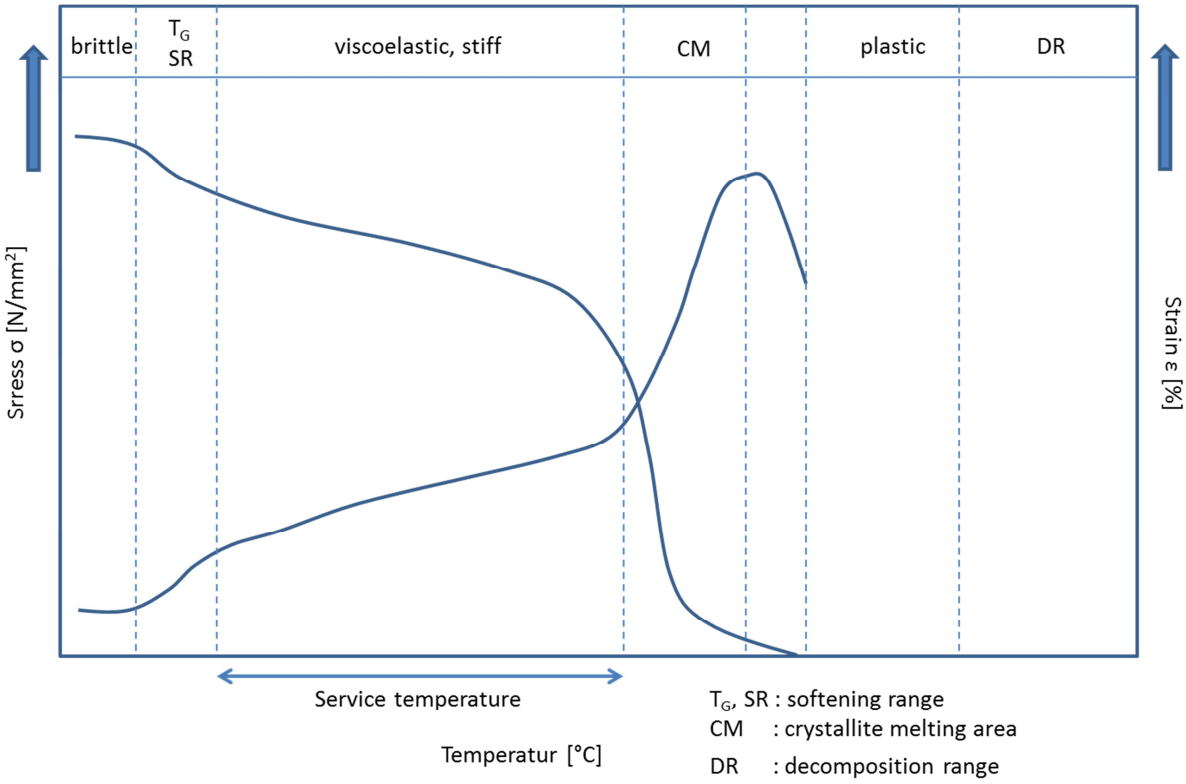


Figure 6-2: Semi-crystalline polymer [28]

The crystalline structure can be observed quite easily by the softening range (T_G) and the crystallite melting area (CM), exemplified in figure 6-2. Above the crystallization melting temperature, which is characertized by a peak temperature of 345°C for PTFE powders and 327°C of sintered products, the material is very transparent, below this temperature it is pure white. [7] Modified PTFE material has smaller crystallites, which scatter the light far less than Standard PTFE. This is why products out of modified PTFE, especially with less wall thickness, seem to be translucent. If thin Standard PTFE or modified PTFE films heated up to 380°C followed by rapid cooling, the amorphous status of the melt is conserved as much as possible, and the films stay transparent. By cooling at slow speed there is enough time for crystallization and the product is milky white. At 19°C there is a crystallite transformation. The different conformations of the molecular chains lead to different formations of crystal lattice: Below 19°C PTFE crystallizes in triclinic formation of chains, above this temperature the short range order is hexagonal. In practice this has two major consequences: sintered products increase the dimensions by approximately 2% when exceeding the crystalline transition temperature of 19°C. Especially for products manufactured within tight dimensional tolerances this is important to know. Not only for finished goods this crystalline transition plays an important role: The free flowing properties and the grain stability of PTFE in the shape of powder and agglomerates clearly improves below 19°C. [7]

For the routine determination of the crystallinity it is important to know, that the density and crystallization grade is proportional to each other. For this reason an easy to perform density measurement for standard specimens will be done. If the whole width of polymer and production impact is considered, densities in the range of 2.120 – 2.190 g/cm^3 exist. The most

important production influence on density and crystallinity of finished products is the cooling speed in °C/min during the sinter process while passing the temperature of recrystallization. For Standard PTFE this temperature for recrystallization is around 312 – 314°C, for modified PTFE around 306 – 308 °C. Some important performance characteristics, for example the mechanical properties, in particular the flexural fatigue properties and the permeability, depend on the crystalline-amorphous propotion. The effectively measured density values at sintered PTFE fall below the theoretical values, as can be seen in figure 7-21, calculated by the composition of the crystalline and amorphous fractions of the polymer. For calculation the following values are used: specific gravity for the crystallites = 2.288 g/cm^3, specific gravity for the amorphous =1.966 g/cm^3. The deviation between calculated and measured values is because of the minor, but really present and measurable pore content of the PTFE. The crystallites are embedded in the amorphous polymer matrix. With regard to the specific gravity of the composed polymer, the disordered transition regions between the crystallites and the amorphous, coiled regions additionally contribute to the measured density values. The amorphous regions give the PTFE its stability, while the crystallites are subject of easily moving layers. This easy sliding of the molecular chains becomes visible in the typical PTFE cold flow. In the group of thermoplastics PTFE has an exceptional position in case of the property distribution of amorphous and crystalline region.This also means that the part of crystalline region within the polymer is high, however they do not contribute to higher stability. The reason is due to the fact that the layers within the crystallites easily slide against each other. The contribution of the crystalline and amorphous regions to the physical properties of the polymer are twisted in comparison to polymers such as polyamid. The easily sliding crystalline layers are the origin for the cold flow of the PTFE materials. The cold flow and the other exceptional properties, as well as the specific high crystalline degree of PTFE are discussed later in detail. [7]

During sintering the residual voids must be eliminated for extreme mechanical properties and resistance to permeation. This means a reduction in the viscosity of PTFE to enable better particle fusion. The measure for this is to polymerize PTFE with a smaller molecular weight or shorter chain length resulting in a lower melt viscosity. Additionally small amounts of comonomer (PPVE) in PTFE disrupts the crystalline structure. [18]

In addition to molecular weight and comonomer content, applying shear force to PTFE can also have an impact on its crystalline composition: One possible important reason for the increase of the crystallinity by the shear-induced alignment of the PTFE submicro-fibrils are found in the wear debris. This is the reason why wear debris shows higher crystallinity compared to the material it is derived from. [2]

6.2 Moulding process for S-PTFE

For the moulding process important parameters are the pressure, the holding time, the cooling and the filling of the tool. The filling of the tool is done with a weight amount or volumetric to a special filling height (free flow material, plates). In any case the powder has to be

distributed homogenious. This is very important in plate production. For perfect parts the whole amount of the powder for the billet must be compacted in one step to avoid billet defects by building up potential splittings and cracks.

To avoid entrapped air, the material should not be compacted too fast. The compaction speed depends substantially from the dimensions of the billet or the compaction ratio of the type of powder. In practice speeds between 10 mm/min and 200 mm/min were approved, whereas the compaction is going to be faster, when the diameter or the wall thickness of the part is small. Between moulding and sintering process the billets should be stored for a sufficient time, in order to have the opportunity for escaping of the entrapped air to come out. For small dimension parts a few hour or one day is enough.

Another important factor is the maximum pressure. It depends on the kind of powder, for compounds also on the kind and amount of filler. It is recommended to have a processing temperature between 21 to 25°C. Temperatures below or above are also possible but for temperatures less than 19°C a 10% higher pressure should be choosen because of the harder particles, which reduce the PTFE flow. Unsufficient pressure can be compensated partially by longer pressure holding time. In this case it is important that while holding time the pressure stays the same. Too low pressure parts often have worse mechanical properties, lower density and a higher amount of pores. Too high pressure produces cracks. To compact sufficient and homogenious, the pressure must be held for a specific time in the range of 5 to 30 min, as can be seen in figure 6-6.

Anyway there are some little differences in the compaction of moulded parts. The density of an unsintered billet is highest at the place where it contacts the pressure plate. This decreases with increasing distance. If sintering pressure differences in the billet are generated, it influences the local shrinkage behaviour. This different shrinkage behaviour can be the reason for cracks in sintered parts. In the range of the recommended pressure all products are very safe in processing. Even deviations of the recommended pressure of about -/+10MPa normally do not effect the properties of the finished product. But if the pressure is reduced too much, the mechanical properties decrease. [1]

Due to processing limitations normally geometric simple shapes are moulded out of PTFE powders. The mostly used tools are of round shape for the production of filled and hollow cylinders. In case the moulding is performed at room temperature, the moulding tools can be made out of carbon steel. The PTFE sided surface must be polished for easy sliding of PTFE and PTFE compounds powder along the wall. In case of a slip-stick-effect while moulding this will first be noticed at the sintered part through the formation of an orange peeling surface. The unsintered green body is showing a total smooth surface even when compacted with slip-stick-effect.

6.2.1 Preforming

Preforming means to charge the mould with the powder and compact it by the application of pressure to prepare a green body with sufficient particle contact and strength to allow handling. Green strength is required because of the steps demoulding from the mould and placement in the oven. The temperature in the moulding process is a variable key. Below the transition temperature of 19°C the material is harder and the powder has better flow properties, but is not well responding to pressure due to its stiffness. If the preforms produced below the transition temperature are manufactured without applying enhanced pressure, they have low green strength and are more likely to crack during sintering. The powder is conditioned at 21 – 25°C for 24 hours to avoid this problem. When the temperature increases PTFE is getting softener and exhibits higher plastic flow and thus can be moulded at lower pressures. For example an increase of temperature from 21°C to >31°C is roughly equivalent to 2 MPa of moulding pressure. The process is excursive and discontinuous and can not be exactely described by a mathematical function. If the press capacity is limited, it can be helpful to make use of this effect of temperature. This means at temperatures exceeding the recommended temperature processing window a decrease in preforming pressure may be necessary to eliminate cracking problems. Uneven fillings lead to non uniform density in the preform and are subject for crack formation. It must be prevented that the resin in the mould should not be precompacted to accomplish room for more powder. This will lead to the formation of a charge line at the interface and possibly may generate cracking during sintering. The mould filling is the step where product contamination in the part is likely to happen. Other process steps where machine oil and dust are present should be eliminated from the moulding areas. To prevent contaminations it is necessary to wipe and clean the exterior of resin drum prior to open and reseal the unused portion of the powder. At the beginning of the moulding step, the powder particles are compacted by rolling and slipping, eliminating interparticle void spaces and removals of air. By the flow of PTFE under pressure the interparticle voids are eliminated. Depending on the dimensions and shape of the billet and the type of resin the pressuration rate is defined. The air-filled void space, which must be eliminated is determinded by the apparent density of the powder.

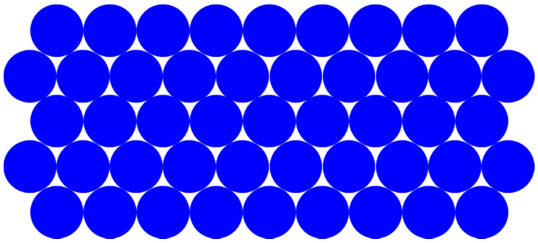


Figure 6-3: Air percentage of 24% in idealized compacted particles

The figure 6-3 above is an idealized picture of round shaped particles, but in practice it is assumed that the air percentage is more than 24%.

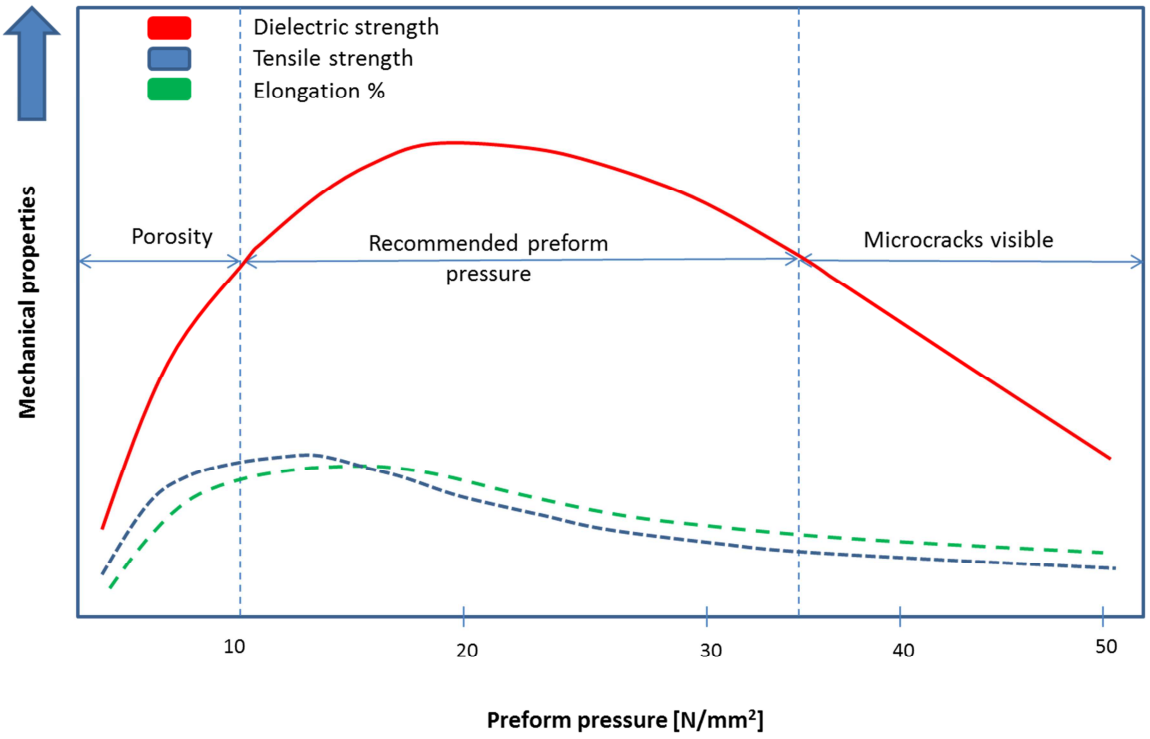


Figure 6-4: Mechanical properties vs. preform pressure [18]

This preforming processing step typically is performed at ambient temperature, preferred 23 to 25°C.

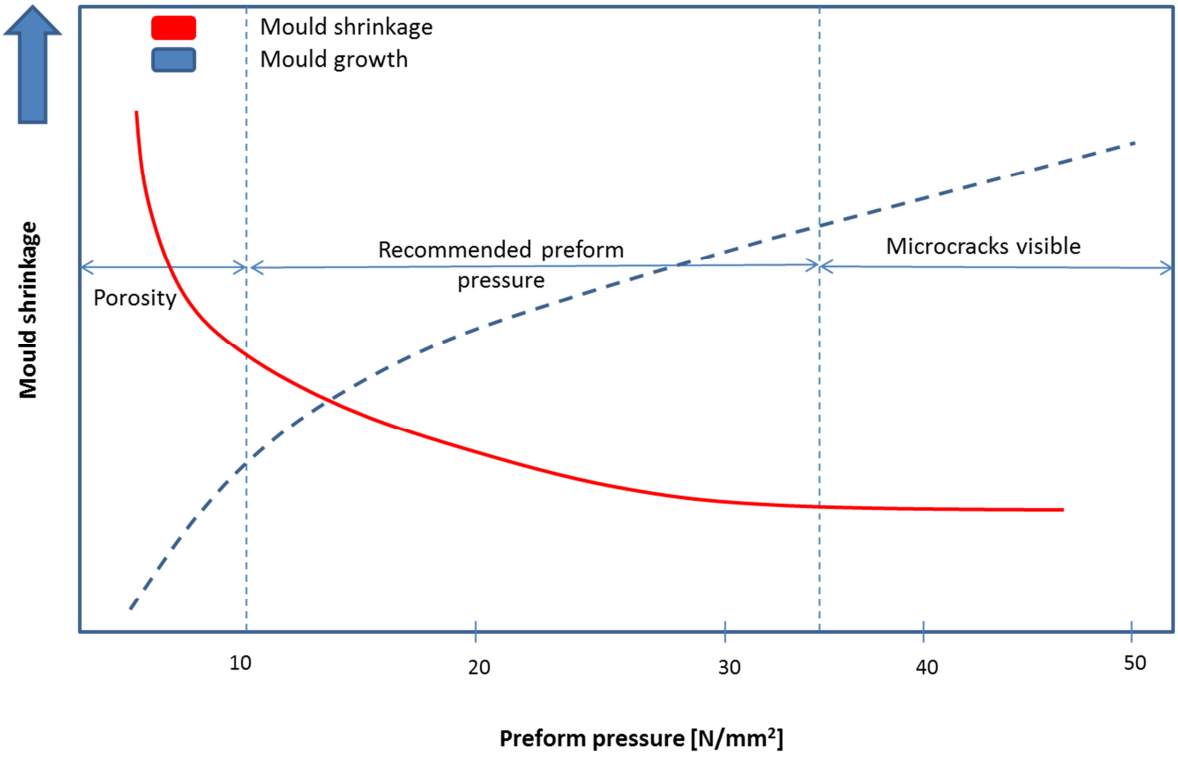


Figure 6-5: Mould shrinkage vs. Preform pressure [18]

The dwell time after reaching maximum pressure is almost as long as the time to reach that pressure. The maximum pressure while preforming has a direct impact on void-closure and the final part properties. Also the shrinkage is strongly effected by the pressure, must be raised as the growth increases. For an even compaction in the preform, the dwell time to avoid cracks, the pressure release has to be started carefully.

In the cross direction the preform has the characteristic to shrink during sintering while it tends to grow in height in machine direction. For reduction of the shrinkage the preform pressure is necessary and an insufficient dwell time leads to density gradients in the billet.

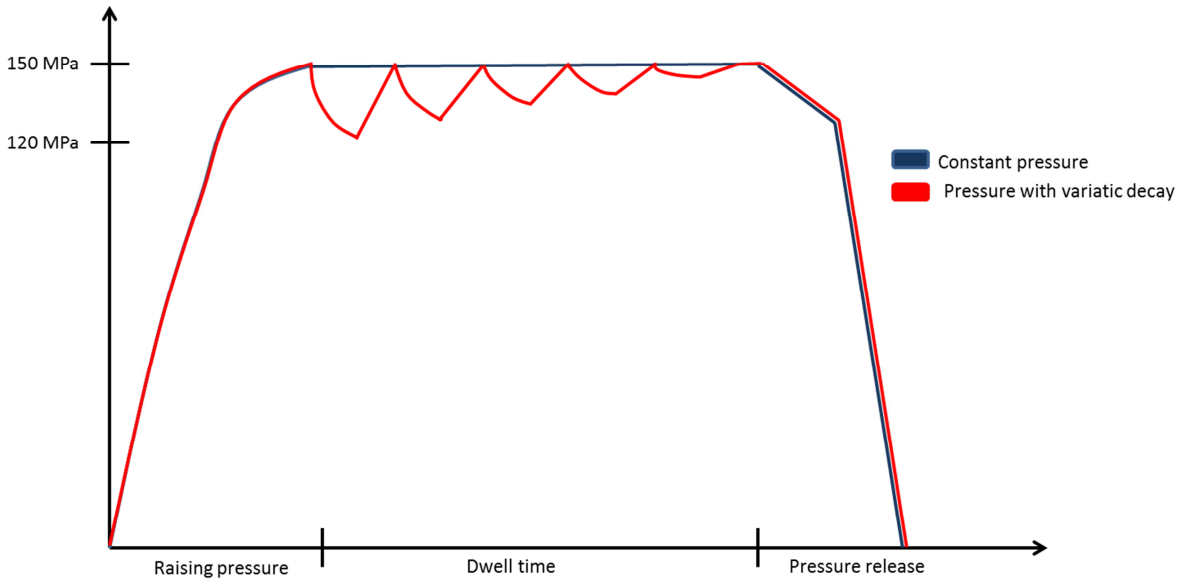


Figure 6-6: Pressure curve

If pressure decay can not be observed anymore the compaction is completed. The flow within the crystalline regions of the PTFE powder become visible by this.
The type of resin, rate of pressurization and the size and shape of the preform determines the dwell time. Releasing the pressure after dwell time should be run slowly until the initial expansion or elastic recovery has taken place. Otherwise visible cracks can be generated because of rapid expansion of the pressurized powder with the entrapped air. The last step for preparation the preform for sintering is the degassing. Entrapped in the preform the air and residual stress remains and should be relieved before sintering. This entrapped air needs time to escape from the preform before sintering. If the air cannot escape from the billet prior to sintering it may cause cracks in the billet. This is the reason why in practice it is recommended to have a dwell time at 280°C for release of the expanding air while the part is still in the non-molten state and thus `open´.

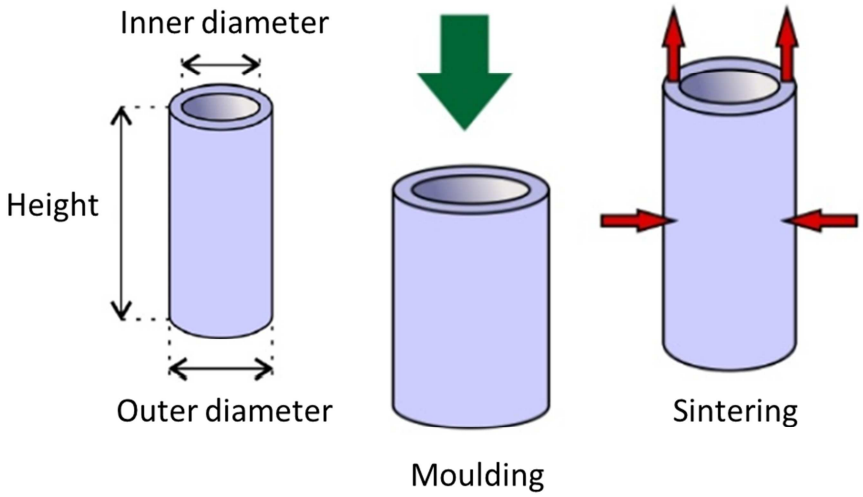


Figure 6-7: Shrinkage at sintering [30]

The figure 6-7 above shows the regular changes in dimension during moulding and sintering. These dimensional changes have to be considered for the design of the moulding tool. [30]

6.2.2 Hydraulic moulding

The hydraulic moulding is the basic method for S-PTFE production for manufacturing simple dimensions. For this method free flow or low flow material will be filled into a moulding form und moulded in axial direction at room temperature, one or both sided. Both sided means that the billet is turned the other way round after half-time to compensate the effects of wall friction. While compacting the air escapes and the PTFE powder particles „flow“, advantaged by the high crystallinity PTFE powders are composed differently with a crystalline content of >94 - 98%. The crystalline content allows powder flow when pressure is applied. The flow behaviour can be detected by ^{19}F resonanz spectroscopy, whereupon particle comprehensive contact is built up. This build up contact across the particle boundaries is the main assumption for the fusion of the particle grains during the following sinter process. Under input of different variations of moulding this method can be used very flexible: The method is suitable for production of small billets for measurements up to producing big dimensioned parts. Generally the filling is done manual. Especially for bigger parts a sufficient pressure supply unit must be ensured. The moulding pressure, randomised to the surface of the moulded part, can be about 70 MPa specific pressure for free flow compounds. [2] This is the pressure applied by the piston to the surface of the billet.

6.2.3 Automatic moulding

The manufacturing of small parts with simple dimensions in big quantities is normally done by automatic moulding. Like the hydraulic presses the automatic presses have a similar setup but with reziprocating automatic working cycles. Also the filling, moulding and discharging is

done automatically. In most cases the manual monitoring is not necessary and it is possible to produce bigger quanities in a very economic way. While production of finished products with automatic moulding it is particularly economic, if the mould is designed in a way that the produced part has reached its final dimension after sintering. [2]

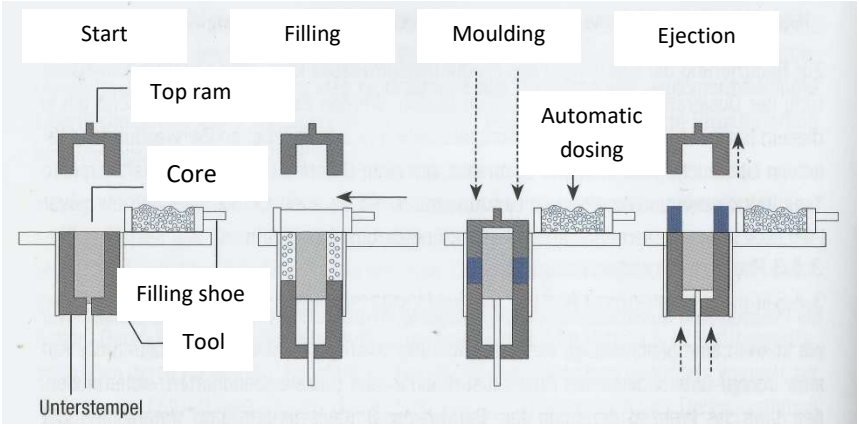


Figure 6-8: Automatic moulding [7]

6.2.4 Isostatic moulding

While at hydraulic moulding the pressure is typically done in axial direction one- or both sided, the pressure influence at isostatic moulding in the uniform pressure is applied from every direction. As pressure transmission medium water is used, which compact the PTFE powder over a rubber membran. In comparison to all other powder approaches and processing technologies getting over the material processing combinations of non free flow powders in connection with isostastic moulding show the best material property results, which is possible through moulding and sintering of PTFE powder. Furthermore isostatic moulding is good for producing parts with complex dimensions, because the moulding form can be configured that the moulded parts will after moulding and sintering come close to the end dimensions. At following machining there is comparable low waste, this means they are close to final dimension. [2]

Comparing the different moulding processes for compaction of the powder hydraulic moulding is the best. For production of big surfaced, thin walled parts (d < 8mm) a press with a little hub is enough. But the pressure must be 15 MPa for low flow PTFE to 35 MPa for free flow material. In case of compounds it is about 70 MPa.

The pressure drop after moulding process must be slowly. If the relaxation is too fast the danger of cracks is given in the moulded block because of the little, but existing relaxation behaviour of moulded PTFE and the resilience of closed rest air in the billet. These cracks are typically across the moulding direction. So the billet is useless. [2]

Defect	Possible cause (in approx. Order of importance)	Suggested correction
Cracks	excessive preform pressure	calibrate pressure, use recommended preform
	too rapid application of preform pressure	reduce pressing rate, particularly last 10% or pressing
	insufficient removal of entrapped air	adjust closing rate, check tolerance between mould shell and end plates (mandrels)
	inadequate degassing	increase degassing time
	preforming a too low temperature	condition resin at 21 - 25° over-night before preforming (min. 21°C)
	uneven mould fill	take care to distribute powder uniformly in die cavity
	poor mould surface	re-machine or polish
	preforming of second charge in an already compressed charge - "tamping"	use mould extension and avoid "tamping"
	too abrupt pressure release	bleed off pressure slowly before full release
	poor fit between mould and extension	redesign or adjust mould and extension for a good fit.
	too rapid heat-up	adjust heat-up rate
	improper mould release	avoid rough handling of preform
	careless handling of preform	avoid rough handling of preform
	moisture in powder	keep drum closed when not in use, particularly when cold resin is brought into warm room for use
	too rapid cool down	adjust cooling rate, introduce hold at 290°C or lower
	thermal degradation	adjust peak temperature/time relationship
Distortion	uneven mould fill	break up resin lumps with scoop, take care to distribute powder uniformaly in mould
	poor joint between mould and extension	insure good fit between mould and extension, compress powder into main mould prior to final pressure application
	poor mould surface	re-machine or polish
	uneven application of pressure	check alignment of moulding tool
	to rapid cooling rate	adjust cooling rate
	"Melt flow" in sintering	use lower sinteirng temperature, especially for modified PTFE
	thermal degradation	use lower sintering temperature and shorter sintering time
	mould shell not concentric bulging during preforming	machine mould to restore concentricity, determine if thicker wall moulds should be used.
Surface roughness	poor fit between mould and extension mould	redesign for good fit, compress powder into main mould before final pressure application
	rough surfaces on mould	smooth mould surfaces
	rust from mould	clean and chrome- or nickel-plate mould
	air entrapment	reduce pressing rate, increase tolerance between end plate and mould shield

Table 6-1: Examples for defects and formations [21]

6.3 Sintering process for S-PTFE

A preform can not be used for real applications because of its limited cohesive strength. Due to sintering it allows coalescence of the resin particles with provided strength and void reduction. Also the sintering cylce and its profile of time and temperature influences the final

properties of the billet. The melting point of PTFE (342°C) is exceeded by sintering temperature in the range from 360°C to 380°C.

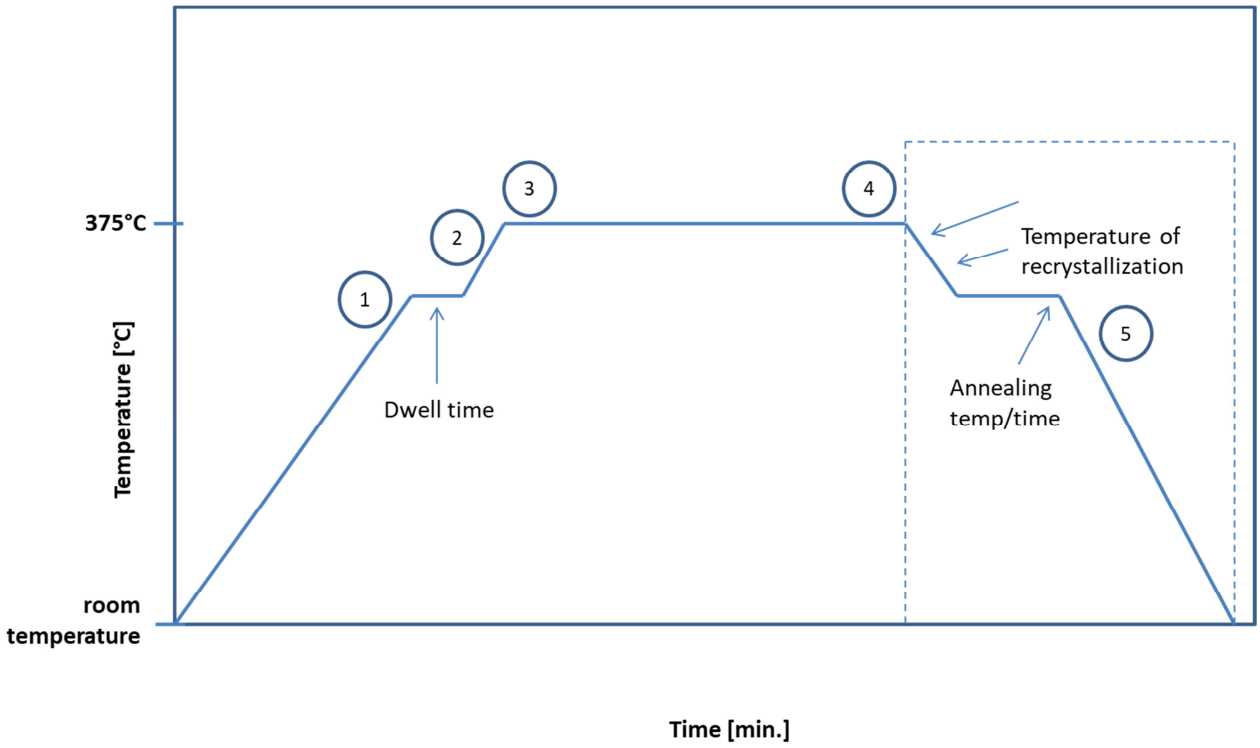


Figure 6-9: A general sintering cycle [18]

There are various steps of the sintering process:

(1) Preform completes its elastic recovery and begins to thermally expand after exceeding the PTFE melting point. Depending on the type of resin, powder, preforming pressure and temperature the expansion can reach up to 25 – 30% by volume.
(2) PTFE is a transparent gel as it is in the „melting phase“, above 342°C. At sintering temperature neighboured molten PTFE particles fuse together and coalesce. After the complete coalesce the two particles are showing the same shape as larger particles and voids are eliminated under the driving force of surface tension (Laplace pressure). [18]
(3) Smaller particle resins and higher preform pressures improve coalesce. Coalesce and void elimination require time because high cell viscosity of the limited mobility of PTFE molecules. Melt creep viscosity of PTFE is in the range of 10^{11}–10^{12} Pas at 380°C which severely inhibits any flow similar to that known for thermoplastics in the molten phase.
(4) The sintering temperature is held for a period of time to allow fusion, coalesce and void elimination to proceed and maximize properties in the part.
(5) A time is reached beyond which the part properties do not improve anymore and is starting degradation. Property development should be balanced against cost in selecting a sintering cycle. [18]

For sintering temperature the specific gravity increases while tensile strength decreases. The molecular weight is lowered when PTFE is degraded above 360°C, which crystallizes more

easily and has decreased tensile strength. Because of the low thermal conductivity the PTFE preform should be heated up slowly. Between the exterior part of the preform and its inside a thermal gradient develops, which is required for heating the interior of the preform.

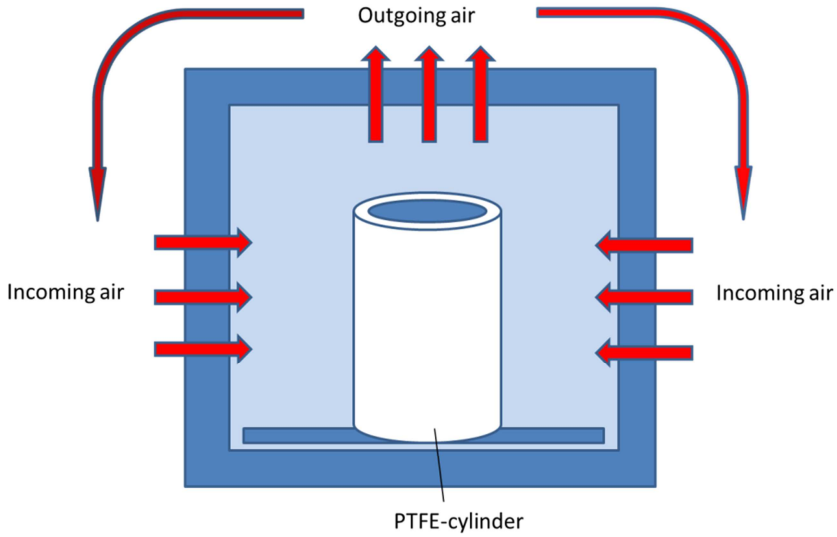


Figure 6-10: Sinter oven, front view

In order to ensure homogenious temperature within the billet, more than half of the complete sintering cycle (in total for PTFE about 20 hours) is used for heating up slowly, especially for large wall thicknesses up to 200 mm. For relaxing residual preforming stresses, which increases as the maximum pressure and mould closing rate increase, thermal treatment is suitable measure. The thermal gradients also induces mechanical stresses in the billet which, along with the residual moulding stress, can surpass the cohesive strength of the preform and lead to its cracking, so the slowest possible rate is the best. The fastest rate is preferred by the economics of sintering, but the compromise is the highest heating rate, which allows relaxation as otherwise internal stresses would generate cracks. This depends on oven temperature, airflow and billet wall thickness (Fig. 6-10). The maximum heating rate should be determined experimentally.

Noticeable is the decreasing heating rate at higher temperatures for massive billets (150 and 300 kg), they can withstand a smaller thermal gradient at higher temperatures. To introduce a number of dwell times at the early stages are a helpful strategy to maximize heating rate, and to allow heating of the interior sections of the part, as can be seen in figure 6-9 and is exemplified table 6-2. It is helpful to reduce the thermal gradient, thus decreasing the probability of cracking. Very important is also the holding temperature near the melting point (>300°C) because of the relatively large volume increase of PTFE. Coalesce and voids in the material is eliminated in the gel state and the rate of sintering near the melting point is low and therefore the maximum temperature is selected above the PTFE melting point. For Standard PTFE the maximum holding temperature is 385°C, for filled materials 370°C. Above these temperatures thermal degradation significantly accelerates so that a typical holding temperature range is 365 – 380 °C. 12 hours holding time at 377 – 382°C have recommendly the best properties and beyond this point properties generally decline. [26]

6.4 Cooling process

The cooling cycle immediately begins at the end of the sintering time and has two important roles – crystallization and annealing of the sintered billet. Many of the properties of PTFE are restrained by the crystalline phase content of the part and the crystallinity is determined by the cooling rate. At 312 – 314°C for Standard PTFE and at 306 – 308°C for modified PTFE the temperature of recrystallization is reached and crystallization takes place. The polymer chains, randomly distributed in the molten state, folded in an ordered structure during the crystallization process. The size and quantity of the crystallites will be higher with slower cooling rate.

Similar to the heating, the cooling is a function of the thermal conductivity of PTFE. It is necessary to cool down slow, especially for thick parts, to avoid large thermal gradient, which can cause cracking of the part. Because of the large volume decrease that the polymer experiences while going from melt to solid phase this is especially important. There is a generation of large stresses in the part, which can fracture the melt if the cooling rate is not sufficiently slow. Furthermore the cooling rate depends on the melt strength and wall thickness. With increasing molecular weight the melt strength of a polymer increases and it can bear a higher thermal gradient. To removal of residual stresses in the billet annealing is referred by holding it for a period of time between 325°C and 290°C during the cooling cycle (between point 4 and 5 in figure 6-9). Furthermore the thermal gradients within the billet are minimized as the billet can follow the exterior air temperature accurately. The annealling temperature also influences the crystallinity of the part. A part annealed below crystallization temperature range will only undergo stress relieve whereas annealing in the crystallization temperature range (300 – 325°C) results in higher crystallinity in addition to stress relieve. This steps are shown in Table 6-2. [18]

The different measurement methods are described in the following chapters for particle distributions, modifier content, tensile properties, density, shrinkage, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The detailed explanation of the different measurements methods can be found in the following chapters.

	from (°C)	to (°C)	hours
1st heating	30	230	5,48
1st isotherm	at	230	1,12
2nd heating	230	280	1,00
2nd isothern	at	280	2,06
3rd heating	280	375	1,00
Plateau	at	375	7,00
1st cooling	at	300	1,25
2nd cooling	300	230	2,00
3rd cooling	230	20	2,00
Total time			**22,91**

Table 6-2: Example for a sintering cycle, other variations are possible

7 Material characterization of different Standard and modified PTFE

After elaboration the basis of the fluorine components, the monomers, comonomers and the well-balanced fluoropoymers, now in the following chapter different Standard and modified PTFE materials will be characterized. For developing a roadmap and in the end to select one Standard and one modified PTFE material for further characterization, the following evaluations have been performed.

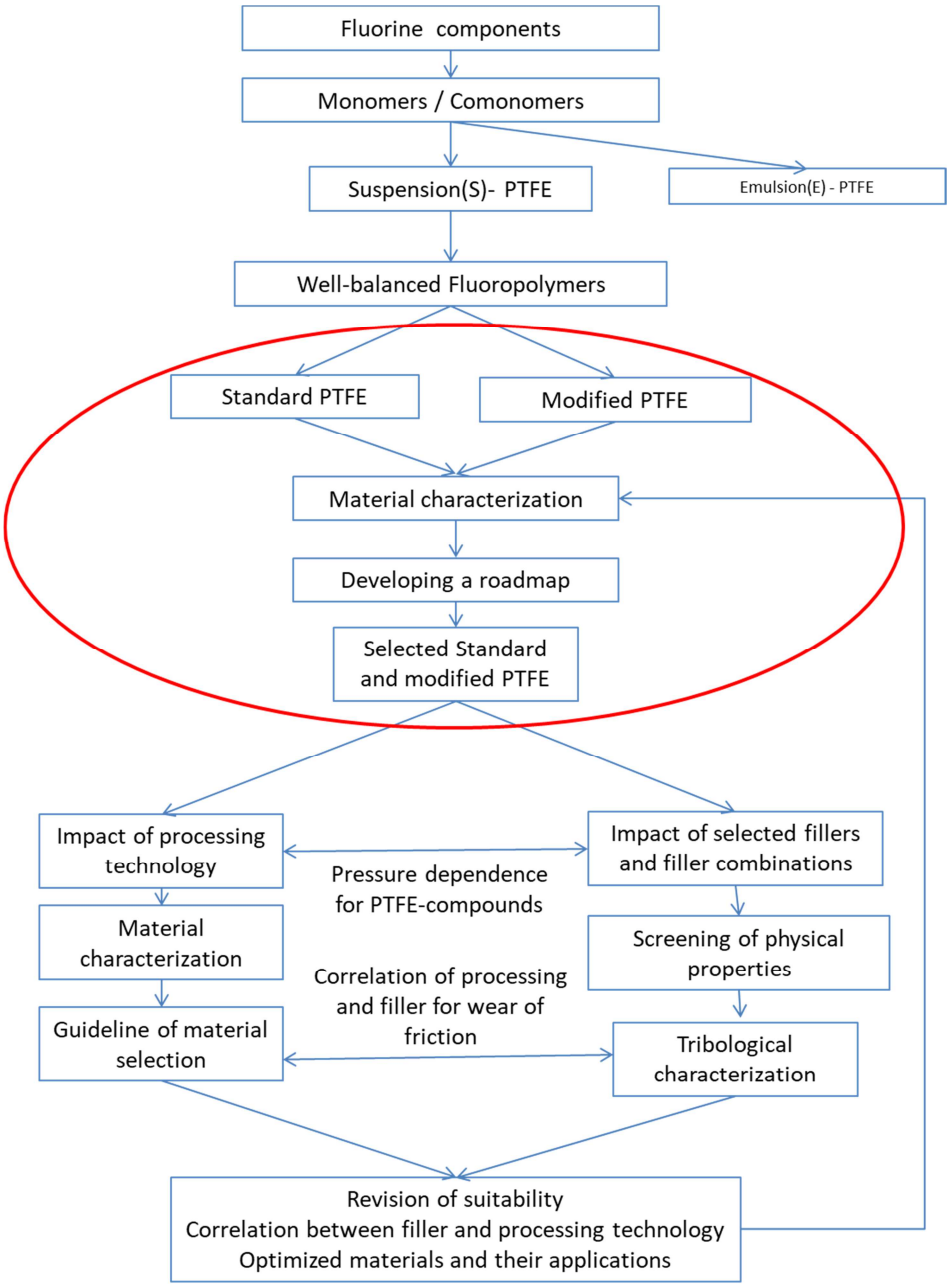


Figure 7-1: Overview of the systematic approach for optimization

Modified PTFE is a chemical modified PTFE with an improved property profile. In difference to the Standard PTFE, beside the comonomer content PPVE, with amounts to 0.05 – 0.1 wt%, also because of its reduced molecular weight, approximitely 20 – 30% of Standard PTFE.

Both factors, well-balanced to each other, lead to a high performance product, which brings out following advantages in comparison to Standard PTFE:

- Reduced deformation under load (cold flow)
- Weldability
- Less porosity, especially important for thin films
- Less tendency for void formation at elongation
- Higher transparency for easier purity control
- Higher elongation at break
- Higher tensile strength at higher temperatures

The better melting behaviour of the particles of modified PTFE during sintering is a consequence of the reduced melting viscosity. Especially due to the reduced cold flow, which generated high internal stresses, processing of modified PTFE can be more complicated the processing of Standard PTFE. This disadvantage of modified PTFE is definitely overcompensated by its special property profile such as tensile strength, E-modulus and others. [30]

In order to investigate the influences of molecular weight, molecular weight distribution and modifier content systematically, initially, for the first time the evaluation the worldwide mostly-known PTFE materials in a systematic way, a total of 15 different grades, with individually balanced modifier contents and molecular weights were analyzed due to their properties under the same conditions. Up to now this kind of material characterization only has been applied for the differentiation between material groups, such as the PTFE and the perfluoralkoxy-polymers (PFAs). The group of the PTFE itself has been analyzed in a systematic way in order to identify the impact of molecular weight and modifier content onto the material properties. As a consequence of this work the clearly described finger print of each individual PTFE material allows the reader to identify the characteristics without the use of any kind of marker. In this work all materials are pressed and sintered under the same conditions and the same kind of test specimen according to the existing standards was used. The comparision of all worldwide modifications gives the opportunity to investigate the materials with specific measurements systematically, the base for the systematic.

		PPVE [wt%]			Molecular Weight [g*mol-1]		
Manufacturer	**Material**	0,000	0,03 - 0,070	0,071 -0,110	270.000 - 900.000	901.000 - 1.400.000	1.401.000 - 3.600.000
	PTFE-MG-1			x	x		
G	**PTFE-MG-2**		x				x
	PTFE-G	x				x	
	PTFE-MC-1			x	x		
C	**PTFE-MC-2**		x				x
	PTFE-C	x					x
A	**PTFE-MA-1**			x	x		
	PTFE-A	x					x
	PTFE-MI-1.1			x		x	
	PTFE-MI-1.2			x	x		
I	**PTFE-MI-2.1**		x		x		
	PTFE-MI-2.2		x		x		
	PTFE-I	x					x
R	**PTFE-MR-1**			x		x	
	PTFE-R	x					x

Table 7-1: Overview on the worldwide set of materials used for the investigation

Molecular weight and modifier content are the major factors to influence the processing behaviour and material properties of the PTFE. If the molecular weight is reduced, melt viscosity decreases and particle fusion during sintering is improved. Unfortunate low molecular weight also enhances the degree of crystallinity of the PTFE polymer thus leading to reduced physical properties. Efficient disturbance of the low molecular weight PTFE during crystallization by an also perfluorinated modifier is required to enhance its amorphous region and provide sufficient physical strength to the material caused by the entanglement of the amorphous regions. To analyze the balancing principles between molecular weight and modifier content applied to the individual PTFE-candidates is another target of this work.

7.1 Impact on powder properties

Because of their polymer structure both, Standard and modified PTFE, are semi-crystalline thermoplastics. Due to the high melt viscosity in the range to $10^{10\text{-}12}$ Pas, these products, however, cannot be processed by means of traditional thermoplastic processes such as injection moulding or melt extrusion. Instead, processing methods have been adapted from the fields of sintered metals and ceramics: The powder materials are first moulded and then sintered to obtain their final properties. Alternatively, special extrusion methods, such as ram- or paste-extrusion, are possible. [18]

7.1.1 Particle size and distribution

The result of Suspension polymerization is rough shaped particles with a variable size, of 1 – 15 mm, and shape and are elongated as a result of vigorous agiation. To convert the polymer into a usable form two processing steps are required. The first step is the removement from water and the polymer should be rinsed and dried. Secondly for reduction of the particle size has to be done before or after drying. The exact details for particle disintegration technology the manufacturer keep it secretely. [18] That means the main contribution to particle formation comes from the polymerization as well as the processing procedure.

The typical average particle size for commercial PTFE powders resulting from the size reduction of the suspension polymer particles are normally in the range of 10 – 50µm. For modified PTFE the processing is the same as for Standard PTFE. [26]

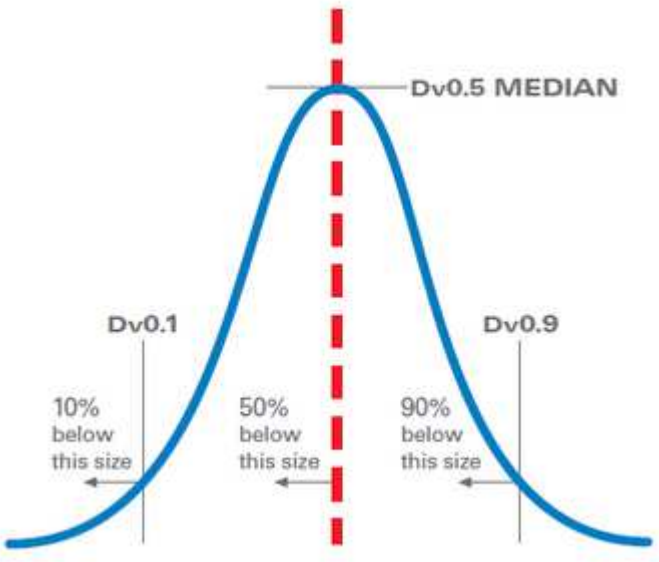


Figure 7-2: Narrow particle size distribution [32]

Many properties of particular materials are influenced by the particle size and are a valuable indicator of quality and performance. The flow and compaction properties are influenced by the size and shape of powder. In comparison to particles with high aspect ratio spherical ones will typically flow more easily. If particle shape is similar, smaller particle powders tend to show worse flowablilty than coarse particle powders. For the typical improvement of Suspension and Emulsion PTFE the following can be stated:

- It is important to measure and control the particle size and distribution of each product to guarantee excellent material properties.
- Free flow properties are better, the rounder and bigger the agglomerates are. The particle size and shape has an influence on the bulk density and flowing properties.

Another reason to control and measure particle size are the industrial and specific applications. In the industry of paint and pigment particle size influence appearence properties including gloss and tinctorial strength.

For the average size a good approach is to report a central point of the distribution along with one or more values to describe the width of distribution. Central values are for example Mean, Median and Mode.

Mean

Similar to the concept of average the Mean is a calculated value. The volume mean can be used to define the central point, although the median is more frequently used than the mean when using this technique.

Median

The Median is defined as the value where half of the population resides above this point, and half resides below this point. For particle size distributions the median is called the d_{50}. The d_{50} is the size in microns that splits the distribution with half above and half below this diameter. Since the primary result from laser diffraction is a volume distribution, the default d_{50} cited is the volume median. This value is one of the easier statistics to understand and also one of the most meaningful for particle size distributions.

Mode

The peak of the frequency distribution is called the mode. For PTFE two aspects are typical:

- For free flow material the distribution is influenced by a final sieving step to reduce the fine and coarse particles
- For low flow material the airjet mills are equipted with a classifier which does not enable the bigger particles to pass. This means only particles with a particle size below 90 – 110 µm leave the mill. So the distribution decreases rapidely in the particle size distribution behind this values.

It is easier to visualize it as the highest peak seen in the distribution.The most commonly found particle size in the distribution is represented by the mode. Normally the mode is not commonly used, but can describe if there is more than one peak to the distribution and than the modes are helpful to describe the mid-point of the different peaks.

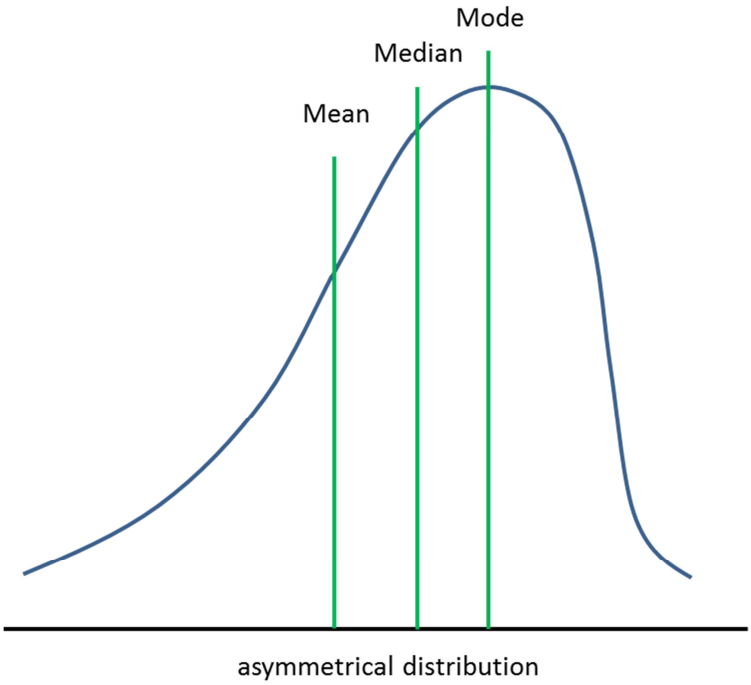


Figure 7-3: The relative positioning of mode, median and mean [52]

As a conclusion the median is the middle number in list, the mean the average of all numbers and the mode is the most frequent number, visualized in figure 7-3.

Distribution widths

For measurement of the particle size distribution instruments with implying an interest on the width of the distribution is used. The field of statistics provides several calculations to describe the width of distributions, and these calculations are sometimes used in the field of particle characterization. The most common calculations are standard deviation and variance. Another common approach to define the distribution width is to cite three values on the x-axis, the d_{10}, d_{50}, and d_{90}. The d_{50}, the median, has been defined above as the diameter where half of the population lies below this value. Similarly, 90 % of the distribution lies below the d_{90}, and 10 % of the population lies below the d_{10} (Fig. 7-2).

All particle size analysis instruments provide the ability to measure and report the particle size distribution of the sample. There are very few applications where a single value is appropriate and representative. Almost all real world samples exist as a distribution of particle sizes and it is recommended to report the width of the distribution for any sample analyzed. The most appropriate option for expressing width is dependent on the technique used. Mostly it makes sense to refer to industry accepted standards such as ISO or ASTM in order to confirm to common practice.

Interpreting results of a particle size measurement requires an understanding of which technique was used and the basis of the calculations. Each technique for particle size determination generates a different result since each system measures based on different physical properties of the sample. Free flow particles are characterized by sieve fractions or liquid laser scattering, while for low flow material the characterization is done by dry laser scattering in air. Once the physical property is measured a calculation of some type generates a representation of a particle size distribution. Some techniques report only a central point and spread of the distribution, others provide greater detail across the upper and lower particle size detected. The particle size distribution can be calculated based on several models: most often as a number or volume/mass distribution.

Different particle sizing techniques, such as laser defraction, sieving and BET, report primary results based on number, volume, weight, surface area or intensity. As a general rule specifications should be based in the format of the primary result for a given technique. Laser diffraction generates results based on volume distributions and any specification should be volume based.

While it is tempting to use a single number to represent a particle size distribution (PSD), and thus the product specification, this is typically not the best way. In nearly every case, a single data point cannot adequately describe a distribution of data points. This can easily lead to misunderstandings and provides no information about the width of the distribution. If forced to use a single calculated number to represent the mid-point of a particle size distribution, then the common practice is to report the median and not the mean. The median is the most

stable calculation generated by laser diffraction and should be the value used for a single point specification in most cases.

The use of a single point in the distribution as a specification is suggested to include other size parameters in order to describe the width of the distribution. In practice two points describe the coarsest and finest parts of the distribution - typically the d_{90} and d_{10}. Like for d_{50} (bulk material), the d_{90} describes the diameter where 90% of the distribution has a smaller particle size (croase particle) and 10% has a larger particle size. The d_{10} diameter has 10% smaller and 90% larger (fine dust). A three point specification will be considered complete and appropriate for most particulate materials (Fig. 7-2). [18]

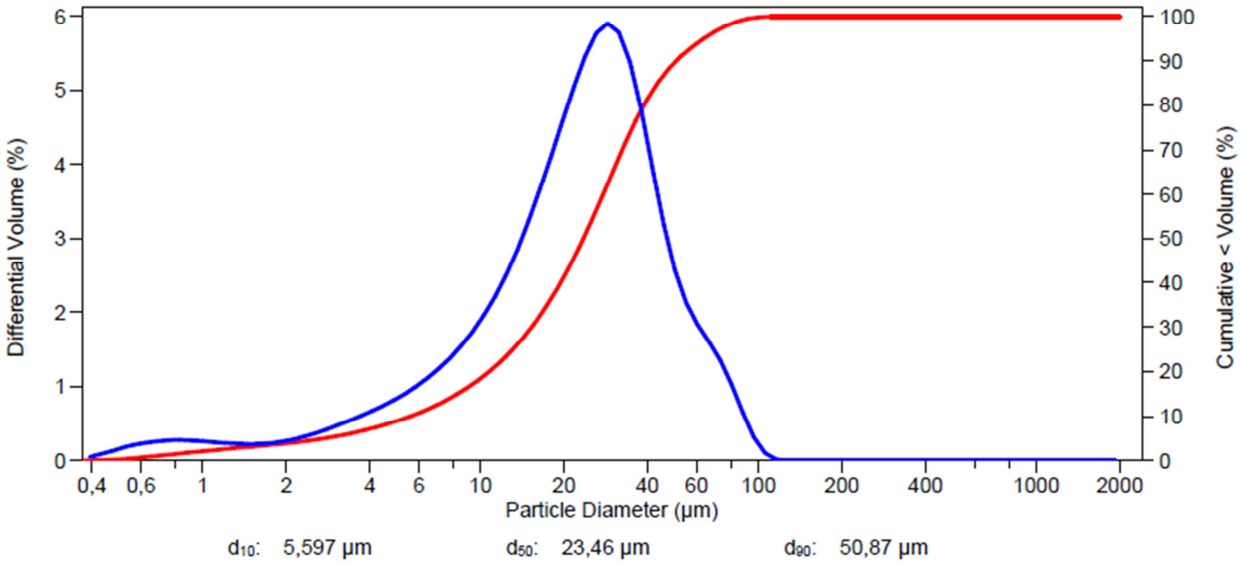


Figure 7-4: Particle size distribution for PTFE-G

The task of setting a particle size specification for a material requires knowledge about which technique will be used for the analysis and how size effects product performance. Sources of error must be investigated and incorporated into the final specification. Be aware that, in general, different particle sizing techniques will produce different results for a variety of reasons including: the physical property being measured, the mathematical model (ball shape, pin or disk) used, the basis of the distribution and the dynamic range of the instrument. Therefore, a specification based on using laser diffraction is not easily compared to expectations from other techniques such as particle counting or sieving. One exception to this rule is the ability of dymanic image analysis to match sieve results. Attempting to reproduce PSD results to investigate whether a material is indeed within a stated specification requires detailed knowledge of how the measurement was acquired including variables such as the refractive index, sampling procedure, sample preparation, amount and power of ultrasound. [33]

The particle size distribution (PSD) in suspension polymerization reactors has a direct effect on the product quality as bigger particles may contain more entrapped chemicals coming from the polyermization recipe. In measurements the PSD would improve the quality

of process models, which should have a subsequent effect on improving the optimization and control of suspension polymerization reactors. Existing techniques, while informative for some systems, have significant limitations. In particular most methods have long time delays before the results of the PSD is available. These delays can be the result of the sample preparation or the actual measurement itself. Different methods for particle size analysis are applicable to different size ranges of the particles. A common offline method to measure the PSD for solid particles is sieving.

Because the processing of PTFE is close to processes employed in powder metallurgy, the characteristics of the powder particles determines the quality of equal cavity filling. In this work particle size and particle size distribution were determined for low flow products in accordance to ISO 13320. All materials were measured and analyzed according to the scattered light method (Beckman Coulter LS Particle Size Analyzer). In addition to the measurement of the particle size a visual inspection was done by microscope. Based on images that show the material in the size range of 100 microns (Fig. 7-5 and 7-6), possible differences were analyzed. Through this all informations are determined und there can be described a cleary influence of the powder form on the properties.

For the consideration of the particle size the general procedure for the manufacturing and processing of PTFE, the d_{50}-value, is used. This median value of a particle collective is considered a representative attribute. It is used as a direct and fast-to-be-determined assessment value. [34] The determination is made from the cumulative distribution curves, as exemplified in Figures 7-5 and 7-6. Of the 15 samples analyzed, almost all types of powder have a d_{50}-value of 21-54 µm. Only the PTFE-(M)R-materials are considerably above 100 µm. The different particle sizes are mainly due to different milling techniques. Generally, in the production of PTFE wet milling is used for coarse grinding and dry milling for fine grinding. Besides the size and size distribution, the grain shape plays a crucial role. The figures of PTFE-MG-1 and PTFE-MR-1 (Fig. 7-7 a and b) compare the significant differences in particle size and particle size distribution. Looking at the distribution curve of the PTFE-MG-1, the measurement results show that the d_{10}-value is about 8,1 µm, while the corresponding value of the PTFE MR-1 is 23 µm (Fig. 7-5 and 7-6). In general the smallest possible particle yields combined with an irregular surface have better material properties. However, too many fine fractions of < 7 µm are worse to work with, because the resulting high specific surface leads to the attraction of dirt and dust forming clusters (PTFE nests and -spots). Similar to the formation of spots and nests the formation of agglomerates can also lead to modified measurement results: In this work it was found that fine particles that are contained in the powder appear in the measurement diagram as a so-called oversize agglomerate, as can be seen in Figure 7-5 at the right shoulder. The speciality of oversize particles is the worse particle coalesence due to higher void volume between the individual agglomerates. Furthermore the mix with fillers is too difficult so that the homogenity is not given.

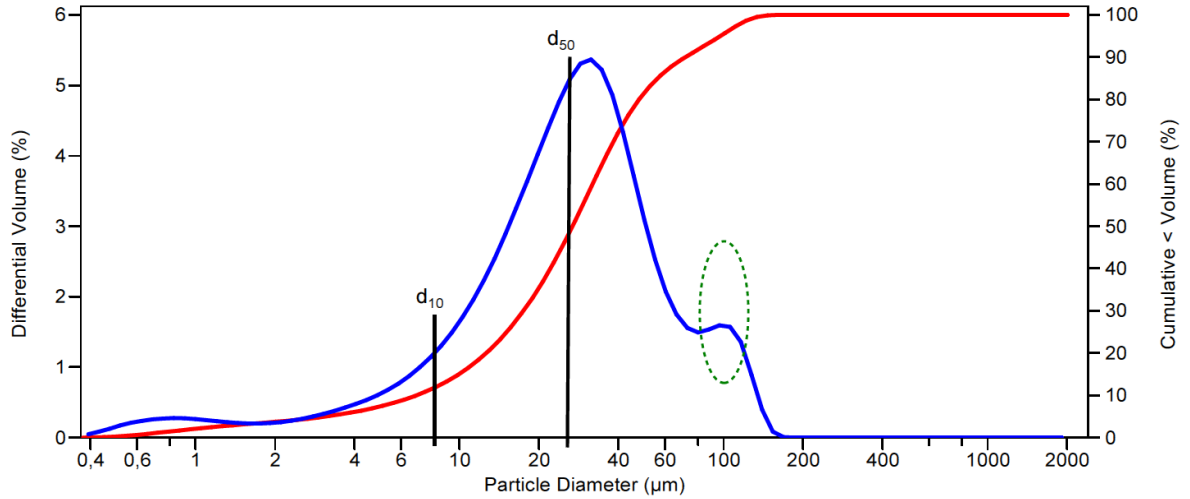


Figure 7-5: Particle distribution curve PTFE-MG-1 measured by the scattered light method (green marked: oversize agglomerate)

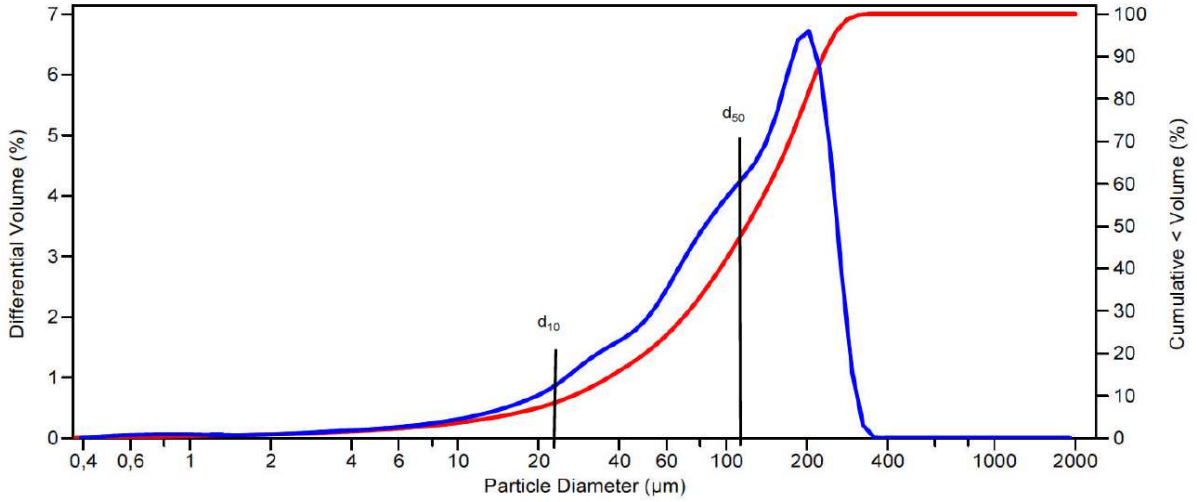


Figure 7-6: Particle distribution curve PTFE-MR-1 measured by the scattered light method

The distribution curve of PTFE-MG-1 in comparison to the distribution curve of PTFE MR-1 shows significant differences in the particle sizes as well as in the distribution. Particle size and particle size distribution have an impact on the blending behaviour for the homogenious mixture with fillers. The median value for PTFE-MG-1 indicates an average particle size of about 29 µm, whereas the median for PTFE-MR-1 is at about 106 µm. In this case, the results can be attributed to the different milling techniques used in the production of the respective polymers. In modified PTFE the modifier content reduces the brittleness of the material to be milled, resulting in a higher energy input required to achieve a comparable particle size result. PTFE MR-1 shows a much steeper slope of the curve to larger particles than PTFE-MG-1 does. Curves of this type result when the actual grinding process is followed by a protective screening that separates coarse particles. Figure 7-5, however, shows the typical curve of an airjet mill with a downstream classifier [6], where the shoulder of the curve at dia. 100 µm can be assigned to the described formation of oversize particles. [48]

7.1.2 Effects of particle shape

As already mentioned, the grain shape has a decisive influence on the mutual fusion of particles during the moulding process. Here the advantages of a finely grinded product are clearly evident.

The increased specific surface enables an improved coalesence of the particles. In addition, a rough surface compared to a smooth one generates a better surface contact during moulding. The complete fusion of the particles occurs during the sintering process, which is subsequent and distinctly separate from the moulding stage, see table 6-2.

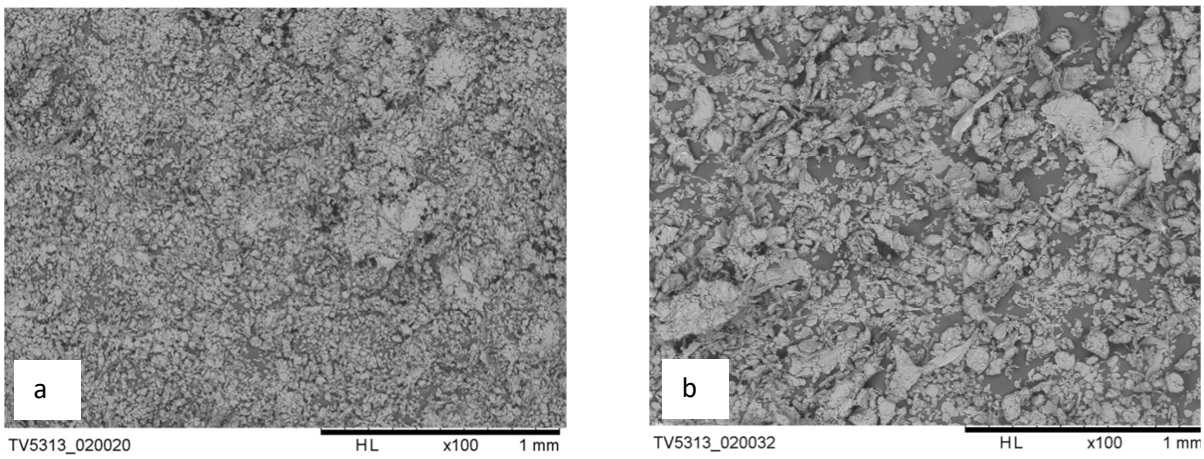


Figure 7-7: a) Powder particles of PTFE-MG-1: small particle size - narrow particle size distribution, b) Powder particles of PTFE-MR-1: croase particle size - broad particle size distribution

As the grinding technology of each material type is specific for its process, and therefore part of each grade of the individual producer, the analysis of the particle size distribution and the shape of the particles is the first indicator for the positioning of the grade in the PTFE roadmap. The particle size and the weight percentage of the d_{10}-fraction of the material are specific for each material type. [48]

7.2 Impact on tensile properties

The mechanical properties of PTFE at room temperature are relatively soft with high elongation at break and used up to permanent service temperature of 260°C. Stress-strain curves are strongly effected by the temperature, as can be seen in figure 7-8. However, even at 260°C the tensile strength is at about 6.5 MPa and elongation at break at about 450%.

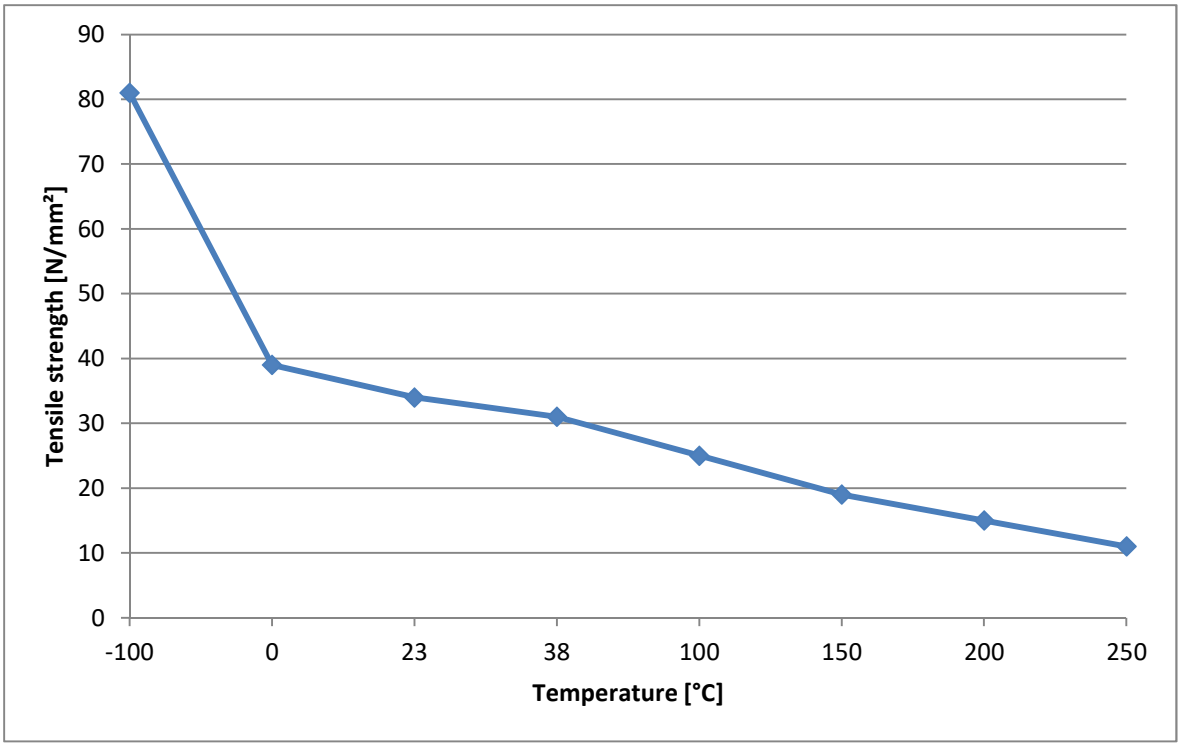


Figure 7-8: Temperature and tensile strength for modified PTFE [18]

Under a sustained load PTFE will creep, which imposes limitations for PTFE in these applications as gasket material between bolted flanges faces. This tendency can be reduced to a big extend by the addition of mineral fillers. These fillers improve the wear resistance but do not have any significant effect on the tensile strength.

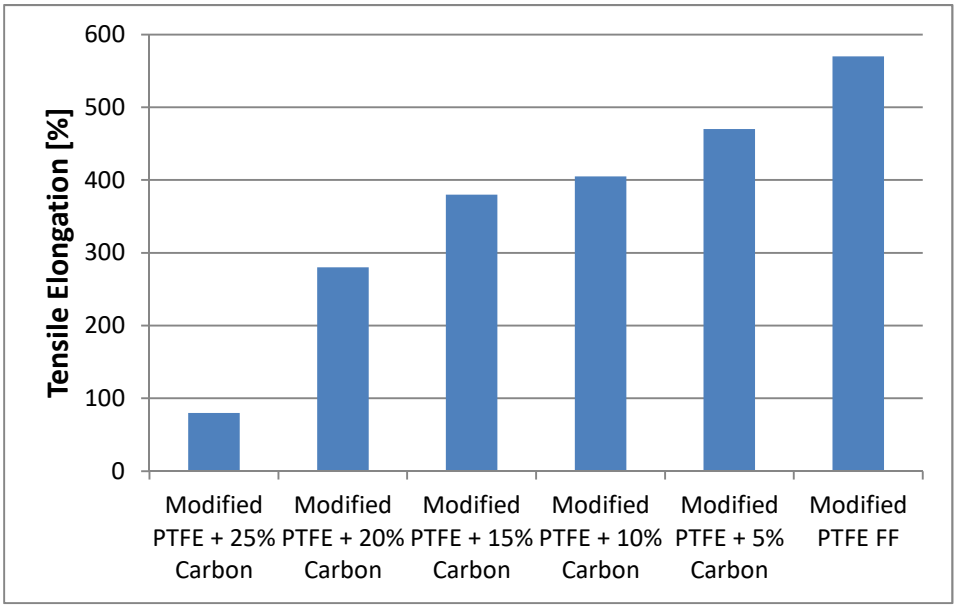


Figure 7-9: Tensile elongation for modified PTFE + Carbon [18]

As can be seen in figure 7-9 the tensile elongation for modified PTFE + Carbon increases with decreasing filler amount.

Generally mechanical properties depend on processing variables like preforming pressure, sintering temperature, time and cooling rate and the degree of crystallinity. Some properties, such as flexibility at low temperature, coefficient of friction and stability at high temperature are relatively independent from the conditions during processing. Flex life, stiffness, impact strength, resilience and permeability depend greatly on moulding and sintering conditions. [35]

For the design of plastic parts and systems these properties are the most important factors:

- The yield deformation decreases as temperature increases
- E-modulus increases significantly with decreasing temperature
- Tensile strength decreases while elongation at break increases with increasing temperature [18]

As soon as the specimens are stretched under load, because of the internal friction there is a temperature enhancement. Because of that reason the strength values decrease and the elongation behaviour changes. Because the deflection of the heat in their surrounding of the specimens with bigger cross section is slower, the thickness of the specimen influences the measurement results.

Characteristic for modified PTFE is the clear picture of a yield strength and the decrease of the tensile strength after passing through. At the beginning the specimen elongation and tensile strength increases again as a result of the strain hardening. PTFE becomes flexible with increasing temperature and therefore the stability decreases. While the tensile strength of the material continouisly decreases with increasing temperature because of the softening, the elongation at break has an increase in the temperature area of 10°C to 30°C, a result of the smooth sliding of the molecular chains against each other until fracture. With following temperature increase the elongation at break decreases again, because release of the molecular entanglement at rising temperature is easier.The distinct yield curve of modified PTFE faciliates the interpretation of the stress-strain-curves a low elongation as can be seen in figure 7-10. As a function of temperature the tensile strength decreases, while the tensile elongation increases with increasing temperature. Additionally in general modified PTFE has higher values than Standard PTFE. [7]

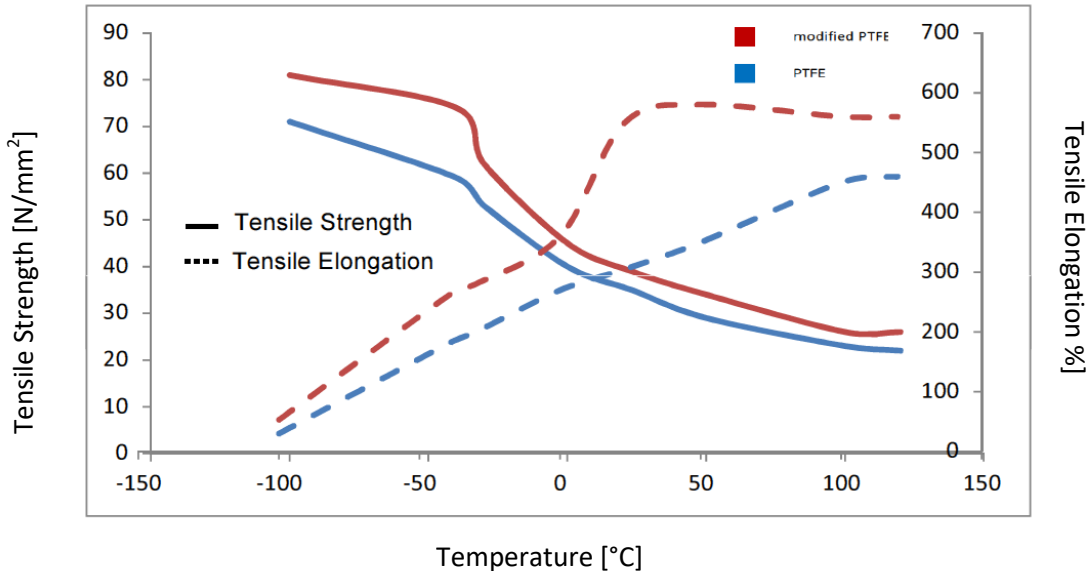


Figure 7-10: General illustration of the stress and strain of PTFE and modified PTFE as a function of temperature [59]

The external effective factors of temperature and surrounding media, the molecular structure, the time, the strain rate and the size of the load have a major role in describing the mechanical properties. [2]

In addition, the degree of crystallization affects the mechanical behaviour. [7] In order to characterize the mechanical properties, polymer manufacturers consider the two parameters of tensile strength and tensile elongation. But for the design engineer additional parameters play an even greater role. These include those polymer properties that describe the behaviour of the material under incipient load up to reaching the yield point.

According to DIN EN ISO 527-3 stress-strain measurements (Instron 5565 H-1509) at a rate of 50 mm/min, which is the standard and generally used for PTFE materials, on SPI-standard FD-105 specimens are run in this work. The reference length on the strain gauge is 22.2 mm and consequently the elongation is determined by applying traverse measurement technique (Fig. 7-11).

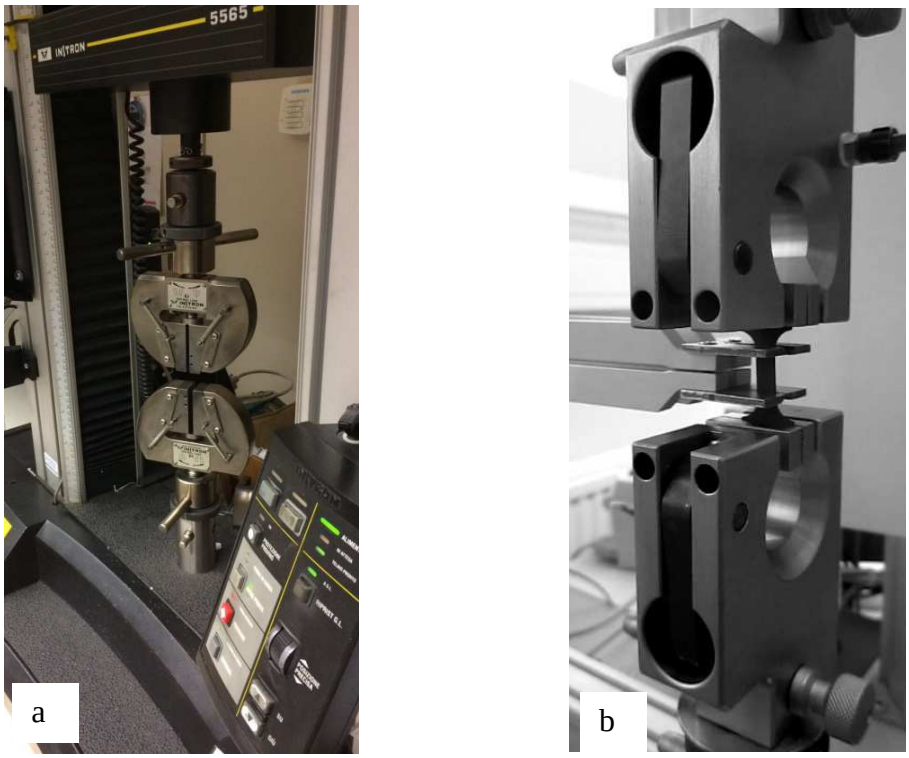


Figure 7-11: a) Traverse measurement (used in this study), b) Measurement with extensometer

Five specimens per material type are stamped out in the moulding direction from 1mm skived film. The minimum values at room temperature (23°C ±2) should be approximately 23 N/mm^2 for the tensile strength and 260% for the tensile elongation. [36]

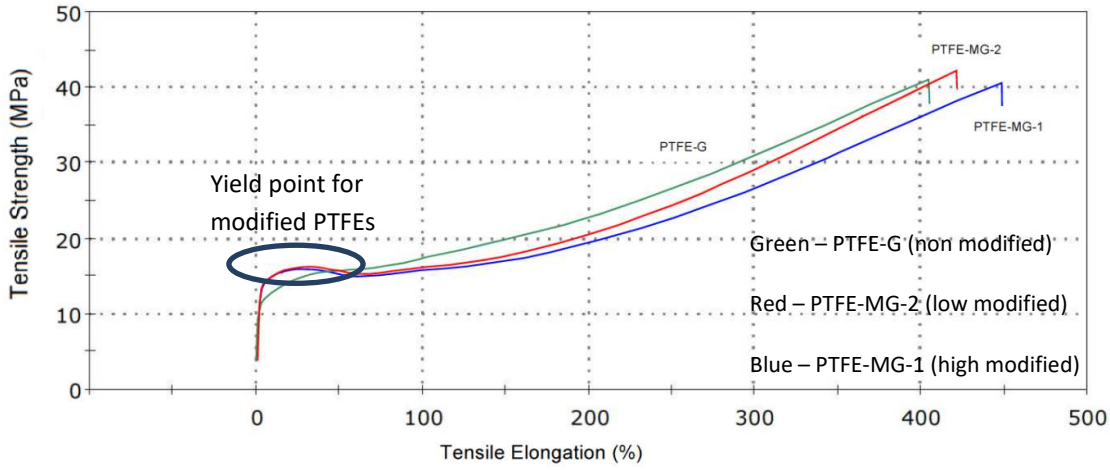


Figure 7-12: Stress-strain curve using the example of PTFE-(M)G-material

As seen in Figure 7-12, Standard PTFE (PTFE-G) points out no defined yield point, and the curve shows a steady increase to break. For modified PTFE the yield strength is clearly marked. After the yield point is exceeded, the stress first falls off and thereafter rises again as a result of strain hardening of the polymer.

The lack or rather the existence of the yield point is interpreted in conjunction with the different size and quantity of the crystallites. Standard PTFE contains of average crystallite

size of 0.15 µm, while modified PTFE has much smaller crystallites with only 0.06 µm, narrowly distributed. The weight percent amount of crystallites which is the range of 60 – 75wt% can be assumed as comparable for both product lines. [7]

In contrast to non-fluorinated semi-crystalline thermoplastics, in which the mechanical strength is defined by the crystalline amount, the strength values for the different types of PTFE can be correlated with the amorphous content. The crystallites of PTFE are constructed from readily mutually displaceable layers, similar to those of graphite. The absence of the yield strength in Standard PTFE thus can be interpreted in that way that flow processes are taking place as the load increases within the crystallites without initially being prevented by the amorphous matrix. With modified PTFE, the situation is different: Due to the excellent embedding of the finely distributed small crystallites in an amorphous matrix a resilient polymer composite is formed within the flow processes, starting directly after exceeding a maximum strain.

This knowledge is obtained by comparing the stress-strain curve of the above Figure 7-12 of PTFE-MG-materials.

The modified PTFE types are characterized by a higher elongation at break (Tab. 7-2). Simultaneously to the integration of a comonomer PPVE, the polymer manufacturers are reducing the molecular weight to achieve the full spectrum of properties of the modified PTFE-types. It would therefore be expected that the modified PTFE-types have reduced values of tensile strength. This expected trend is observed only at PTFE-MI and PTFE-MR-1 products. The fully modified PTFE spectrum of properties is defined as the combination of the advantages of the low molecular weights with the good mechanical properties of high molecular weight PTFE. For all other modified PTFE-types the strength values of the unmodified variant were met or even exceeded, a consequence of the well-balanced effects of modifiers and molecular weight. Figure 7-12 show the yield strength and the permanent increase in strain.

Material	PPVE [wt%]	Ø-Particle diameter [µm]	Shrinkage [%]	Density [g/cm³]	
	internal	ISO13320	ASTM D 4894	DIN EN ISO 12086	
PTFE-MG-1	0,104	29,1	6,20	2,16	
PTFE-MG-2	0,052	40	5,87	2,16	
PTFE-G	0,000	23,46	4,17	2,16	
PTFE-MC-1	0,081	22,69	5,27	2,17	
PTFE-MC-2	0,066	41,79	5,11	2,14	
PTFE-C	0,000	51,57	4,41	2,17	
PTFE-MA-1	0,082	53,99	6,45	2,16	
PTFE-A	0,000	38,97	4,25	2,15	
PTFE-MI-1.1	0,084	24,45	5,74	2,16	
PTFE-MI-1.2	0,108	25	6,77	2,17	
PTFE-MI-2.1	0,066	22,09	6,59	2,18	
PTFE-MI-2.2	0,036	21,15	6,44	2,17	
PTFE-I	0,000	30,82	4,52	2,14	
PTFE-MR-1	0,073	106	6,96	2,16	
PTFE-R	0,000	119	4,46	2,14	

Material	Tensile elongation [%]	Tensile strength [MPa]	E-Modulus [MPa]	Shore D	Ball-Hardness [N/mm²]
	DIN EN ISO 527-3	DIN EN ISO 527-3	DIN EN ISO 527-3	DIN EN ISO 868	DIN ISO 2039 Part 1
PTFE-MG-1	461,76	41,34	624,74	166,49	34,42
PTFE-MG-2	434,22	43,41	596,50	160,32	32,18
PTFE-G	401,67	40,36	530,76	143,23	29,74
PTFE-MC-1	518,71	45,55	608,32	171,83	34,48
PTFE-MC-2	390,79	41,09	515,63	142,37	30,08
PTFE-C	340,87	40,86	403,04	120,42	27,72
PTFE-MA-1	461,93	42,57	611,71	168,41	34,14
PTFE-A	342,48	41,11	428,12	122,44	27,72
PTFE-MI-1.1	433,18	38,44	504,46	144,07	33,80
PTFE-MI-1.2	543,52	36,03	646,27	179,98	38,50
PTFE-MI-2.1	507,10	34,13	656,46	175,52	37,70
PTFE-MI-2.2	541,08	37,10	642,21	178,60	37,80
PTFE-I	323,26	39,19	392,77	113,24	27,48
PTFE-MR-1	338,78	31,11	506,66	141,68	31,20
PTFE-R	225,32	30,91	389,46	110,19	26,38

Table 7-2: Summary of the measurements carried out under this work (excluding DSC and DMA)

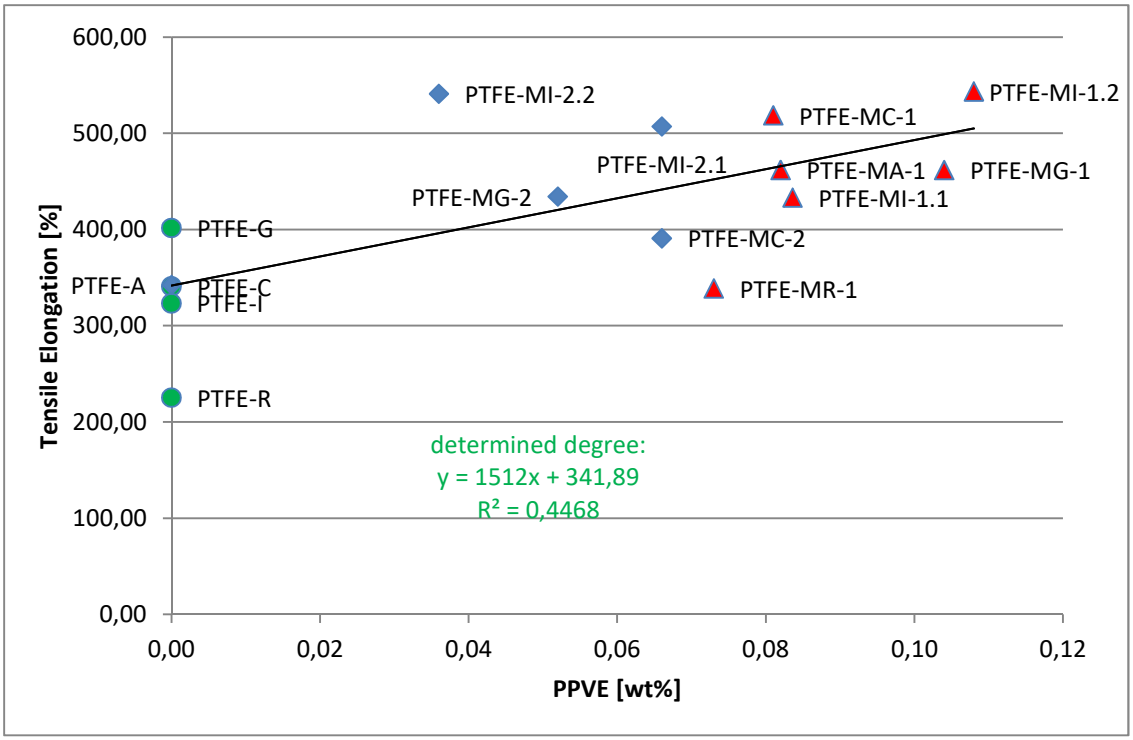


Figure 7-13: The increase of tensile elongation with increasing PPVE content

Figure 7-13 desrcibes the correlation between tensile elongation and PPVE content. The determination of PPVE is a comparable precise measurement method, whereas the tensile elongation is a sensitive indicator which can underlie at break large variations. This is because entanglements and voids have a strong influence. The Standard PTFE grades are in the range of 200% - 400% whereas the tensile elongation increases the more PPVE is contained. An exception is the highly modified PTFE-MR-1, which, in relation to the other modified grades, shows low tensile elongation but significant higher that PTFE-R. The origin of this exception could be identified by analysis of the recrystallization behaviour by using DSC-method: The polymerization process is performed in a way that not all polymer fractions really showed the characteristic properties of modified PTFE. As a matter of fact the temperature of recrystallization for the grade PTFE-MR-1 shows a broad range from 300°C – 315°C. Apart from that all types of PTFE follow in principle the theory that, inter alia, the tensile properties are improved with increasing PPVE content. The cause for the increase in strength values with increasing PPVE content can be seen in the increased molecular entanglement of the amorphous area as a result of the crystallization-disruptive factor PPVE. The observed increased tensile elongation can be explained only through the simultaneous presence of an amount of low molecular weight material. These facilitate the easy mutual sliding of the molecular chains without interfering on the entanglement mechanisms. As described in this chapter, besides the PPVE content also other factors influence tensile elongation. Therefore in figure 7-13 a very broad scattering range is observed.

The balancing of molecular weight and modifier content, monomodal molecular weight distribution and statistical incorporation of PPVE assumed, defines the position of the

individual PTFE-grade with respect to tensile strength and elongation within the PTFE roadmap.

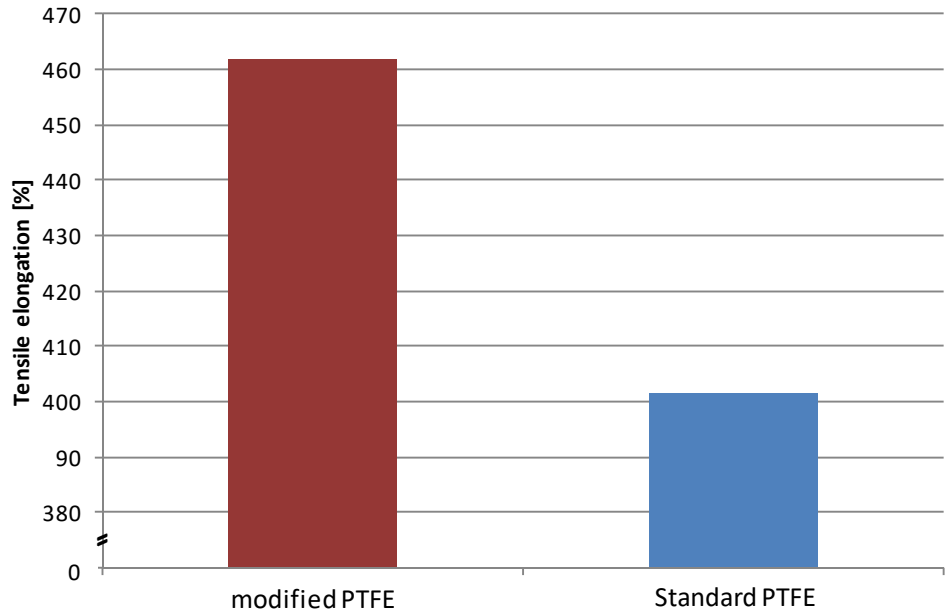


Figure 7-14: Comparison of tensile elongation for modified and Standard PTFE

E-modulus

Standard PTFE and modified PTFE can be considered as energy-elastic polymers in the range of very small strains (< 1% elongation).

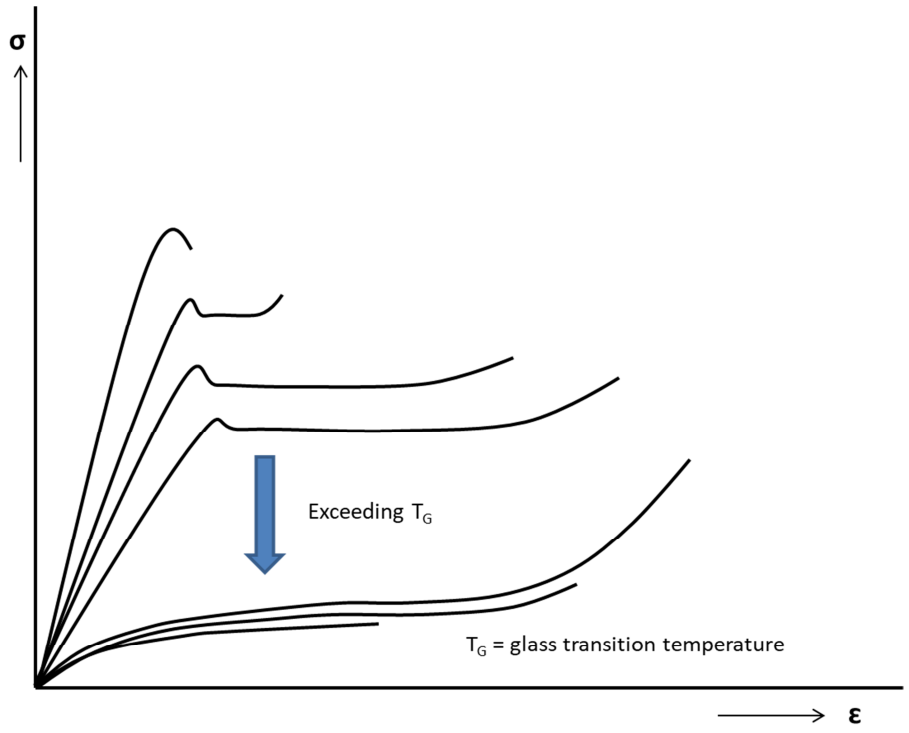


Figure 7-15: Stress-strain curves for semi-crystalline polymers at different temperatures – at testing temperature below glass transition temperature (T_G) no yield point is observed [55]

DIN EN ISO 527-1 recommends determining the Young's modulus as the secant between the strain values of 0.05% and 0.25%. The strain rate for the determination of the modulus of elasticity is 1 mm / min, which is only 2% of the scanning speed applied for the determination of tensile strength and elongation at break. In the range of 0.05 – 0.25% for measurements it is not possible to use the standard strain rate of 50 mm/min and reduce to 1 mm/min according to DIN EN ISO 527-1. Because of the softness of the material PTFE and the comparatively small cross-section of the specimen FD-105, the initial pre-load force applied in this case is only 3N. [48]

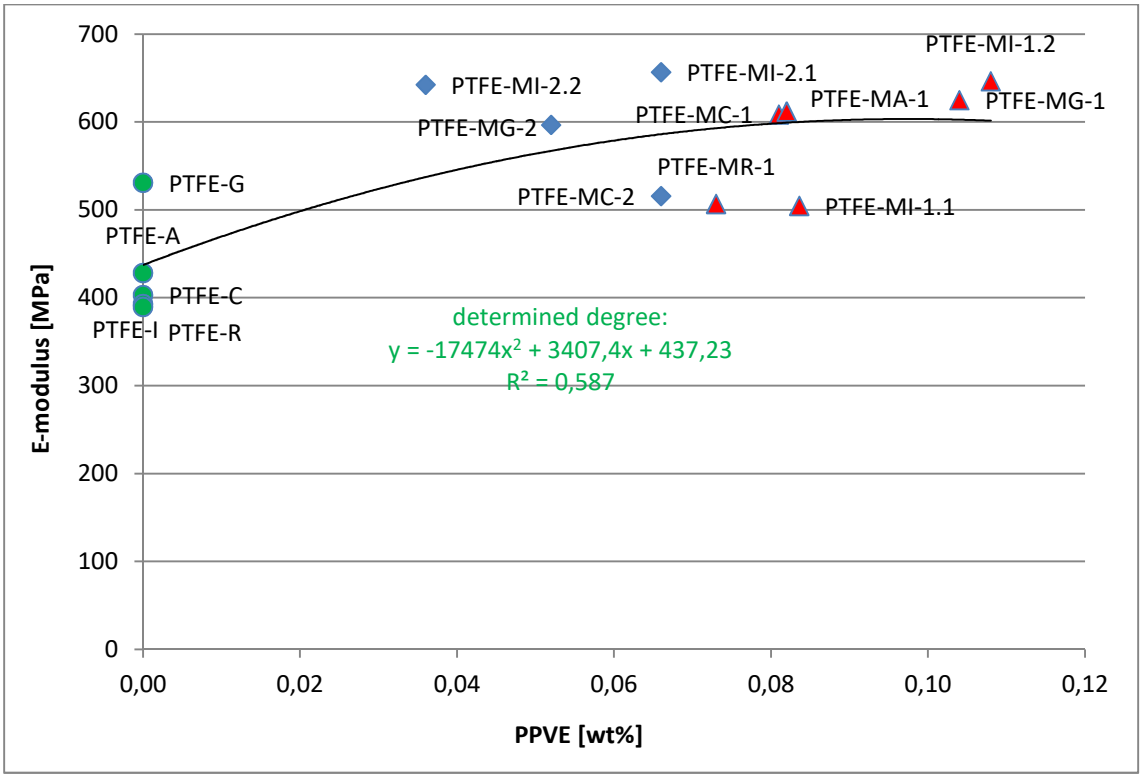


Figure 7-16: Modified PTFE types tend to have a higher E-modulus than Standard PTFE types

Figure 7-16 describes the correlation between E-modulus and PPVE content. As described in this chapter, besides the PPVE content also other factors influence E-modulus. Therefore in figure 7-16 a broader scattering range is observed.

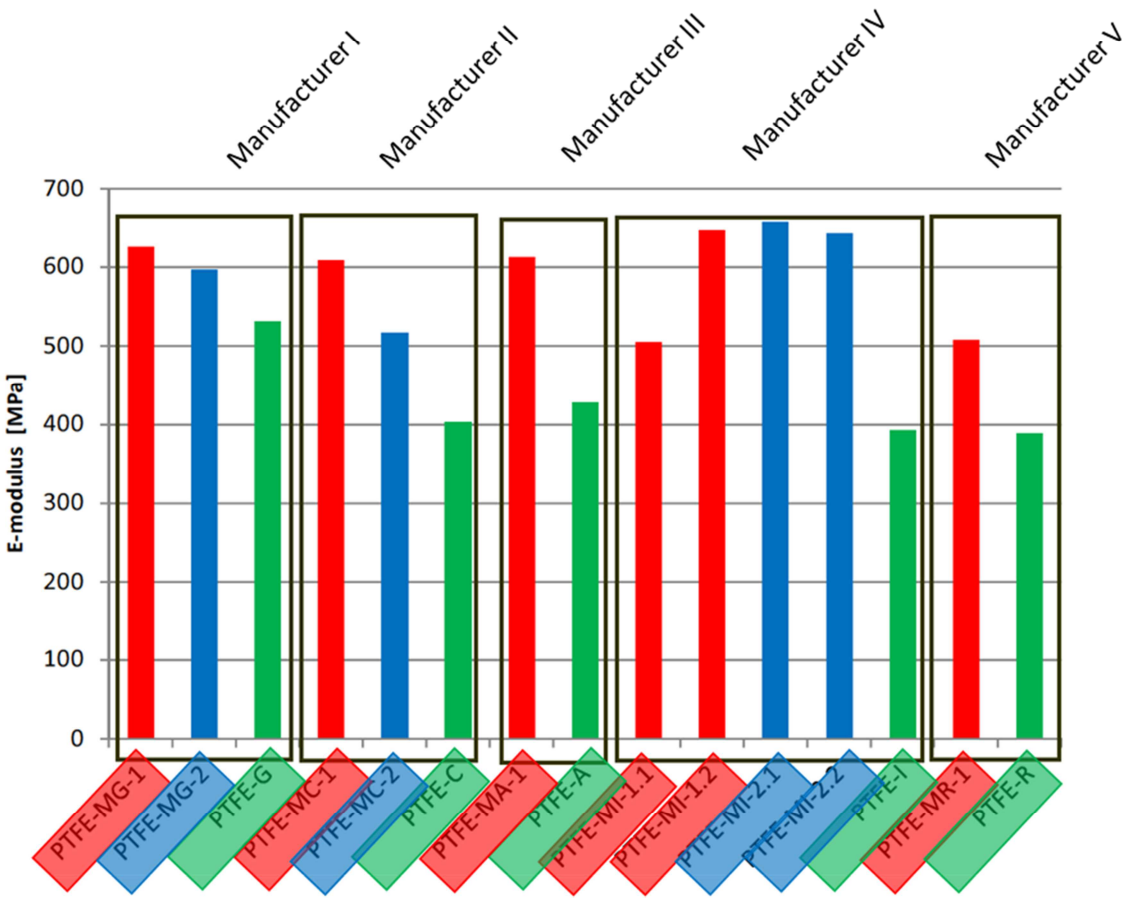


Figure 7-17: History of the Young's modulus (Red: high-modified PTFE, Blue: low- modified PTFE, Green: unmodified PTFE) grouped by manufacturer (black boxes)

Similar to the modulus of elasticity, the tensile stress at 0.5% elongation also shows higher values for the modified PTFE grades. In particular, the PTFE-(M)I-products are noticable for particularly high tensile stress values. This is true for both the high (PTFE-MI-1.1 and PTFE-MI-1.2), and the low-modified PTFE products (PTFE-MI-2.1 and PTFE-MI-2.2). The PTFE-MG-1 has a strikingly low tensile strength, but a high elastic modulus value at 0.5%, which is explained later in detail. [48]

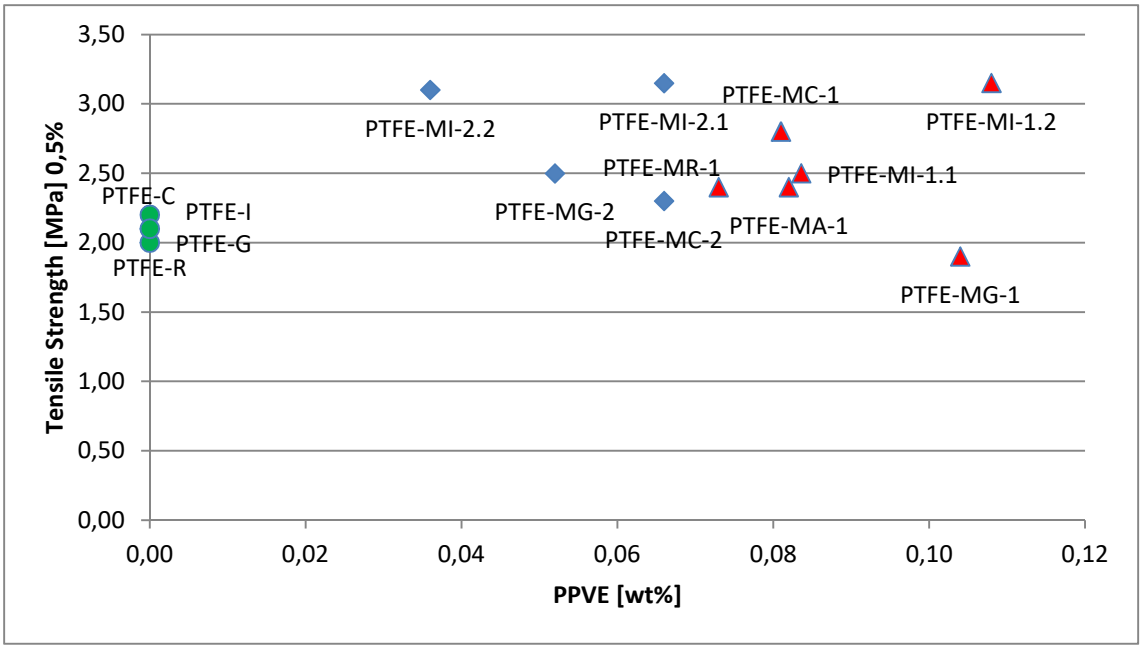


Figure 7-18: Tensile strength at 0.5% elongation of materials of various PPVE-content

Figure 7-18 above shows in terms of colour the differences between the Standard (green), the low-modified (blue) and the highly-modified PTFE-types (red). It follows from this that the difference between the different material modifications of the modified grades within the "Hooke's" characteristics of the stress-/strain curve is not well established yet. However it becomes clearly visible that the E-modulus of the Standard cluster turns out to be the lowest values.

7.3 Impact on modifier content

For PTFE PPVE contents higher than 0.5 wt% are superfluous, because the combination of excellent mechanical properties and melt-processability can already be realized at PPVE contents below 0.5 wt%. The lower PPVE contents have the advantage to comprise the thermal stability to a reduced extent than observed for PFA and significantly reduces the costs of the raw material. [37]

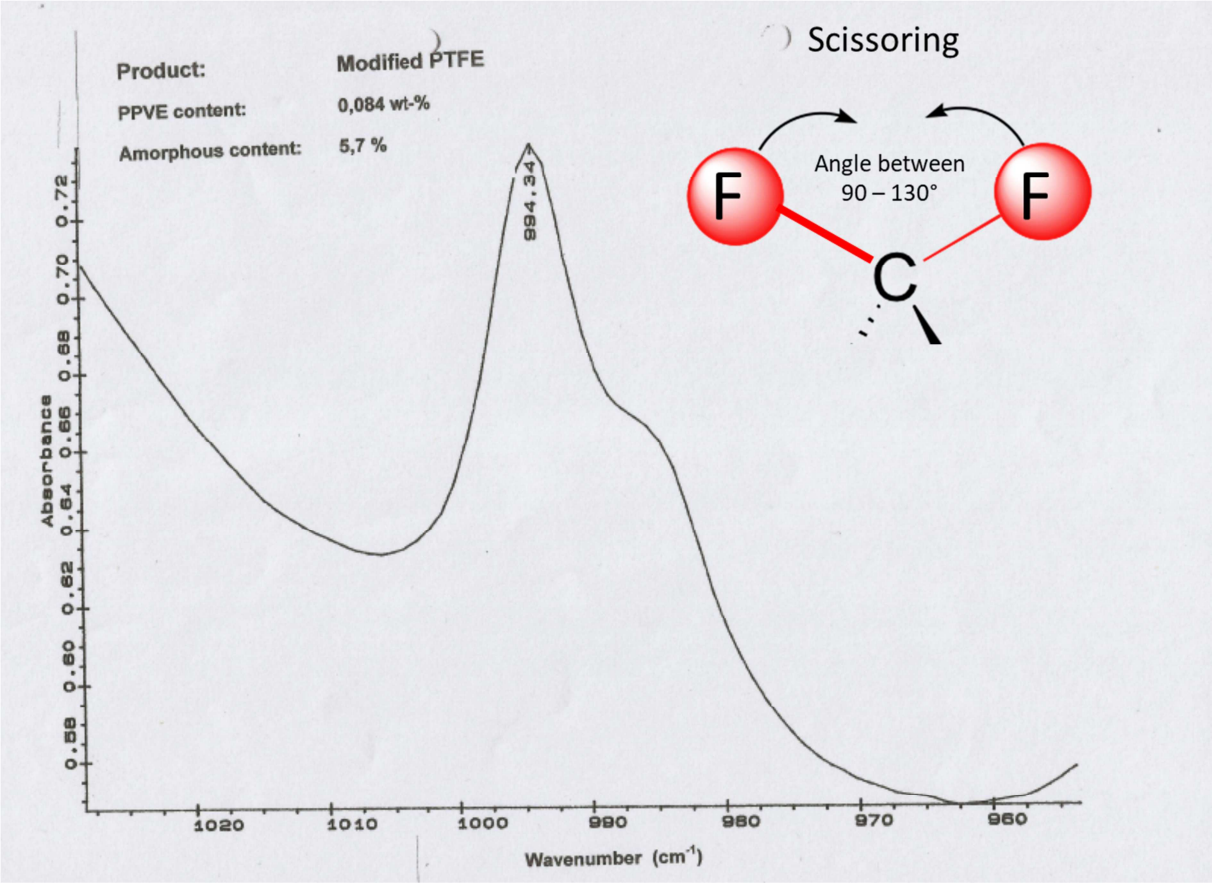


Figure 7-19: PPVE peak at 994 cm^{-1} with bending oscillation [31]

In modified PTFE the content of the modifier can be determined by infrared spectroscopy using one of the CF_2-vibrations. The extremely low levels require application of the Fourier-transform-technique (JASCO FT/IR-4200TypeA). To determine the content of the comonomer PPVE in the film samples in transmitted light technique, scans (recommended scan number >15) in the momentum range of approximately 450 to 4000 cm^{-1} were recorded. The PPVE content is identified by the ratio of the height of the PPVE-peaks at 994 cm^{-1} and the reference peak at 2365 cm^{-1}. In order to determine the value of the comonomer the following formula was applied:

(Height PPVE-Peak/Height reference-Peak) * 0.95 = wt - %PPVE (7.1)

As a reference peak a main peak out of the crystalline phase of fluorine polymers is used at 2365 cm^{-1}. For the determination of the quantity of the modifier the C-F-valence oscillation of the CF_2-group next to oxygen is used. This valence oscillation generates two signals at 1340 cm^{-1} and 994 cm^{-1}.

The 994 cm^{-1}-bend is preferred for the determination due to little overlapping with other oscillations of the finger print region of PTFE.

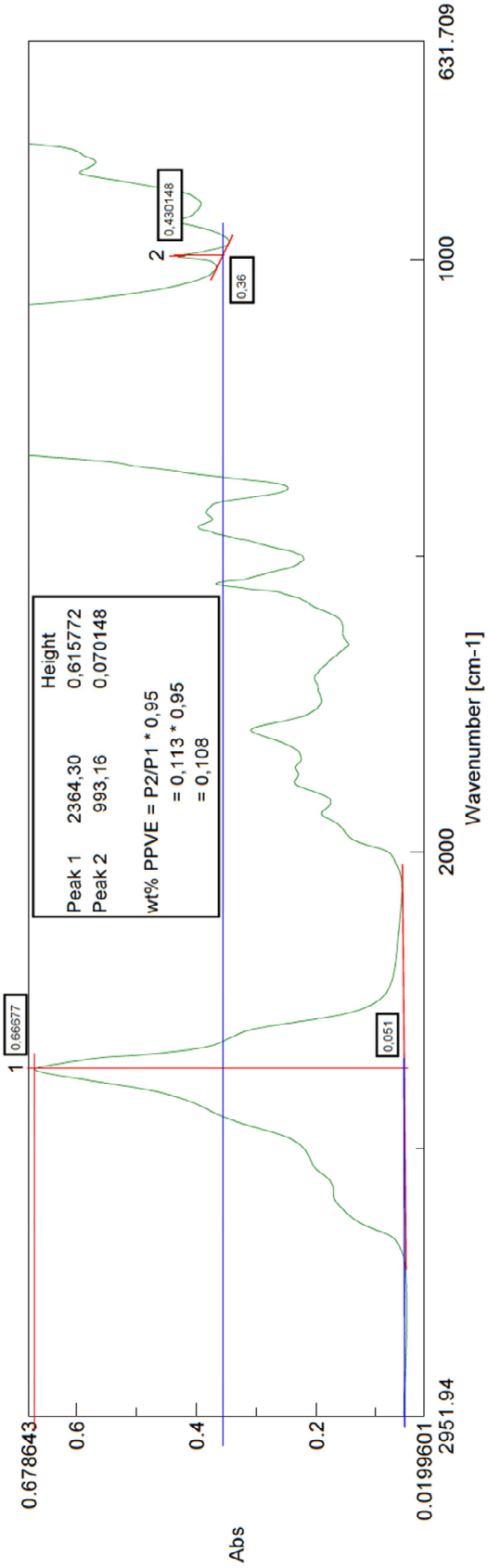


Figure 7-20: Peak measurement of the FT-IR determination of PPVE contents exemplified by PTFE-MI-1.2

Modified PTFE types with small amounts of PPVE were first developed by HOECHST AG. [39]

The PPVE content of these types of PTFE lies between 0.05 and 0.1 wt%, which reduces the gap between the linear homopolymer PTFE and perfluoroalkoxy co-polymer (PFA), with a typical content of 3 to 4 wt%. In order to determine the PPVE the FT-IR method is employed using a 0.1 mm thick skived film. The purpose of these measurements is to demonstrate that the contents of highly modified PTFE types of all manufacturers are between 0.071 to 0.110 wt%. For the low-modified PTFE types, this margin is 0.030 to 0.070 wt%. Furthermore, it is noticeable that there are manufacturers with very tight specification limits regarding the PPVE contents, while others produce within very wide limits, e.g. PTFE-MI and PTFE-MR materials.

The FT-IR method is an excellent technique to determine the very small amounts of the modifier PPVE. However no information is given by this method about the way how the modifier is incorporated in the molecules, randomly, strictly alternating or blockwise. Taking the Q-e parameters (Q ≙ resonance energy, e ≙ induced charge) of the monomers TFE and PPVE into consideration randomly incorporation should be preferred. With respect to the polymer manufacturers different widths of specification limits and preferred average values can be observed. This is an additional hint to determine the source of the polymer and also for positioning in the roadmap. [48]

7.4 Impact on molecular structure and density

Modified PTFE grades are reduced in molecular weight by a factor of about 5, thus enabling an excellent particle fusion during sintering, a prerequisite for the well-known advantages of modified PTFE. Normally, the reduced molecular weight would result in an increased crystalline fraction because of easier chain folding, which would have a negative impact on the mechanical properties. However, the polymerized modifier PPVE interferes effectively with the increased tendency towards crystallization of low molecular weight modified PTFE. Thus, the union of the advantages of low molecular weight PTFE with the high mechanical strength of Standard PTFE succeeds.

The crystalline portions of PTFE have a density of 2.288 g/cm³, the density of the amorphous portions is 1.966 g/ cm³. The resulting density of the semi-crystalline PTFE is derived from the rule of mixtures, ideally with no voids. Therefore, the density test is to determine the crystalline/amorphous ratio of PTFE.

As in the case of modified PTFE this ratio is determined on the one hand by the molecular weight and on the other hand by the modifier content, separate measurement series should be used for conclusions about the molecular weight impact for both product lines.

The density test is performed in accordance with DIN EN ISO 12086 by the buoyancy method (Mettler Analytical Balance Scales). This digital measuring device determines the density of the specimen by measuring it first in air and then in distilled water admixed with a wetting agent (PERVITRO 75%) in order to, among other things, avoid bubble formation on the test specimen. Since the density increases with increasing degree of crystallization, and the degree of crystallization and the molecular weight are inversely proportional, the high molecular weight samples show a lower density than the low molecular weight ones.

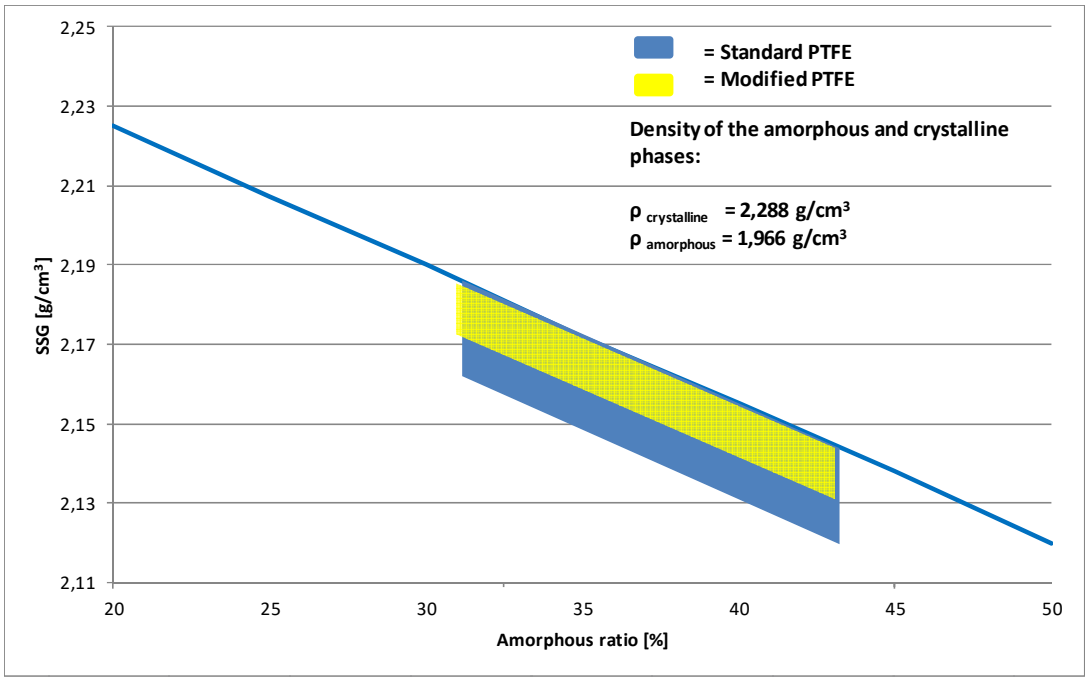


Figure 7-21: Typical density ranges (SSG: Standard Specific Gravity) of Standard and modified S-PTFE, depending on the crystalline / amorphous ratio with lower void volume

The underlying amorphous contents in Figure 7-21 were determined by differential scanning calorimetry (DSC), through which the amorphous contents of the polymers can be determined quantitatively. It is a relative method, which can be calibrated by means of X-ray data on the absolute values of the crystalline content. [37] By combination of density and DSC measurements, the calculation of molecular weight is possible using the following formula:

$$M_n = 3.39 * 10^{13}\ \Delta H_C^{-5,16} \qquad [26] \qquad (7.2)$$

In these investigations, a relative method was used to determine the molecular weight of the PTFE materials, as due to its insolubility in organic solvents below its melting point, there is still no reliable method available to absolutely determine the molecular weight of high molecular weight PTFE. In former approaches, the so-called stoichiometric molecular weight [26] was calculated from kinetic considerations of the polymerization reaction. Based on this method, the maximum possible molecular weight of Standard PTFE was reported to be in the range up to 10^8 g*mol^{-1} while the modified PTFE typically is characterized by a molecular weight of 20% of this value. The relative method as described in this work with the max. average molecular weight of 3.6 *10^6 g*mol^{-1} measured reports significantly lower values. The main reason for the difference should be caused by the fact, that average numbers are

being measured by the applied methods while max. possible values had been the result of the former kinetic calculations. [37] Furthermore, the range of the average molecular weight of the modified grades reaches values far below the originally mentioned 20 %. [26] The producers of modified PTFE, as it cleary becomes visible by analyzing their products, follow different concepts in balancing PPVE content and molecular weight.

This yields the following values:

	Delta H [J/g]	Density [g/cm³]	M_n [g*mol^{-1}]
PTFE-MG-1	29,7	2,16	852.661
PTFE-MG-2	26,4	2,16	1.565.754
PTFE-G	26,9	2,16	1.421.274
PTFE-MC-1	30,3	2,17	769.052
PTFE-MC-2	24,4	2,14	2.351.084
PTFE-C	25,3	2,17	1.950.284
PTFE-MA-1	31,2	2,16	661.244
PTFE-A	24,4	2,15	2.351.084
PTFE-MI-1.1	27,7	2,16	1.221.811
PTFE-MI-1.2	34,4	2,17	399.538
PTFE-MI-2.1	36,9	2,18	278.191
PTFE-MI-2.2	36,5	2,17	294.285
PTFE-I	23,6	2,14	2.792.375
PTFE-MR-1	27,4	2,16	1.292.429
PTFE-R	22,5	2,14	3.572.218

Table 7-3: Calculating the molecular weight on the basis of density and DSC data (Δ H * is enthalpy of fusion of the first heating of the sintered product)

The Standard PTFE types on average are showing the highest molecular weight. The highly-modified PTFE grades have the lowest molecular weight, while the pattern formed by the low-modified grades is not uniform. Due to the special method of calculation (scattering light method) two materials, PTFE-MC-2 and PTFE-A, obviously have the same molecular weight. PTFE-R has the highest calculated molecular weight.

The exception here is the PTFE-MC-2, which despite the modification shows an extremely high molecular weight. In the market it is also known as the modified PTFE with excellent flexural fatigue properties. This property is a direct consequence of the high molecular weight. [7]

PTFE-MI-2.1 and PTFE-MI-2.2 combine a low modifier content with the lowest molecular weights in the sample range. This is confirmed by the high values of the melting enthalpy at the first heating in an ideal way, and also explains the low tensile strength values. PTFE-R is the product with the highest of all the calculated molecular weights. Its melt viscosity is correspondingly high, whereas particle fusion is possible only to a limited extent; the lowest density of all products measured is the logical consequence. PTFE-C stands out in the group

of Standard PTFE due to its high density. Consequently, an increased value for the enthalpy of fusion during the DSC analysis would be expected as a result of the associated high crystallinity. However, this is not the case. But the other values, such as in particular the modulus of elasticity, cannot confirm this special position either. It should therefore be clarified in further studies whether the obviously inconsistent individual readings could be the result of a very broad or bimodal molecular weight distribution.

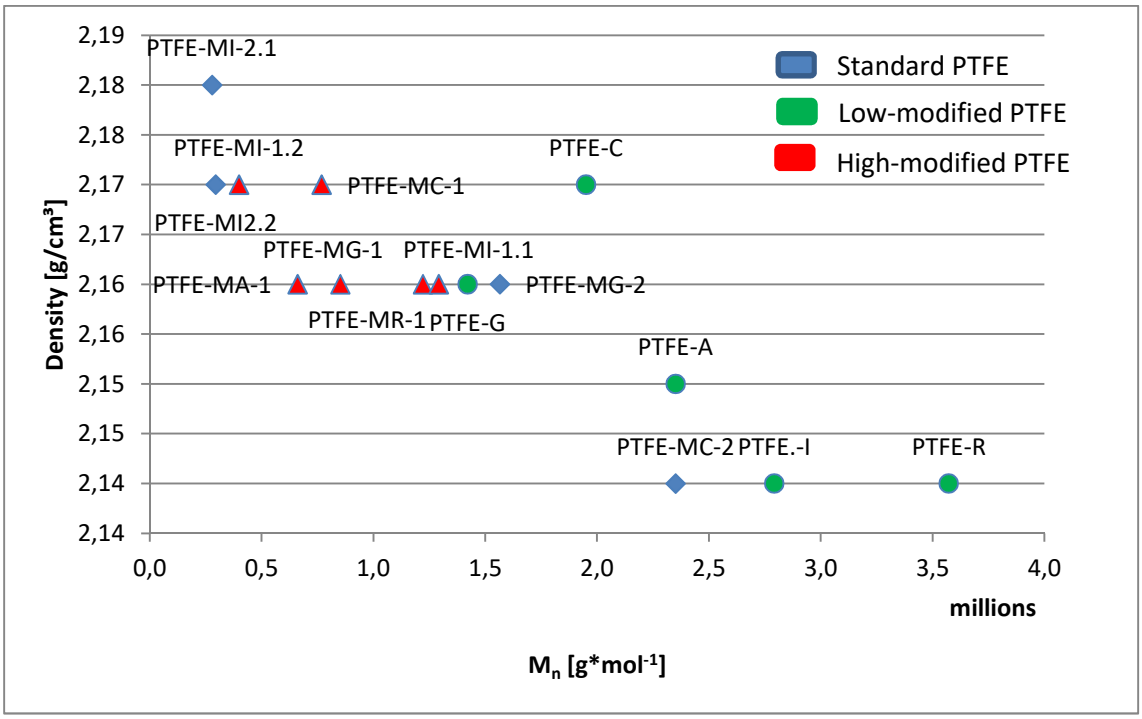


Figure 7-22: Overview of the density and molecular weight of the three product groups: Standard PTFE (green), low-modified PTFE (blue) and high-modified PTFE (red)

The density of semi-crystalline PTFE polymers is influenced by the chemical composition as well as by the processing parameters. As processing parameters have been standardized, only the impact of molecular composition onto the density is discussed. The test results clearly show, that the highly modified PTFE materials are pretty close to each other with respect to density and molecular weight. However the low- and Standard PTFE materials show a broad diversification. Materials such as PTFE-C or PTFE-R can be clearly distinguished by density and molecular weight only. They obviously are manufactured by very unique technology and recipe. [48]

7.5 Differential Scanning Calorimetry Analysis (DSC)

In the DSC method, the first heating of the sample is going up to 370 °C. The crystallite melting peak in this sintered PTFE (about 327 °C) is used for characterization of the material. In case of powder (unsintered PTFE) the crystallite melting area is 342 °C – 345 °C due to the greatly increased crystallinity and the comparatively larger crystallites, a consequence of

undisturbed crystal growth in an aqueous medium under polymerization conditions. The temperature range of the crystallite melting curve (°C) and the enthalpy of fusion (J / g) are determined. Through the determined values of the first heating, the specifics of the product with regard to sintering during processing are detected. [40]

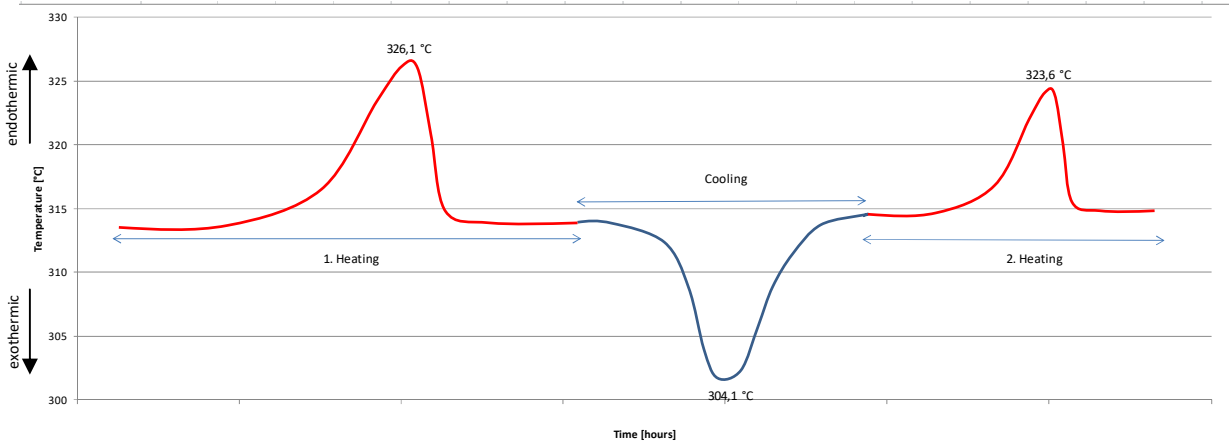


Figure 7-23: DSC: Heat-cool-heat-curve

For the most accurate recording of the PTFE phase transformations, calibration with indium and zinc is recommended. The PTFE samples have a weight of about 10 mg and are punched to obtain a flat bearing surface of a film of appropriate strength. They are placed in an aluminum bin which is closed with a perforated aluminum cover. Samples with significantly higher mass would result in signal shifts (systematic error) due to the delay in heating, while samples << 10 mg result in an increase in the statistical error due to the unfavourable signal-to-noise ratio. The measurements refer to a temperature range from room temperature to 360 °C, using a rate of 10 K / min-1 (1st heating, cooling, 2nd heating) both for the heating as well as for the cooling, to get information about the complete melting and crystallization behaviour (Fig. 7-23). The quantitative evaluation of the heating peaks is based on the temperature range from 280 °C - 345 °C. The cooling peaks are evaluated with temperature limits of 325 °C – 260 °C.

The degree of crystallinity X^C is calculated by the equation

$$X^C=\Delta H^f / \Delta H^f{}_0 \qquad (7.3)$$

in which ΔH^f is the energy content of the transition (the enthalpy of fusion) of the sample and $H^f{}_0$ is the maximum achievable theoretical value of the 100 % crystalline sample. The calculation assumes a value of 82 $J*g^{-1}$ for $H^f{}_0$. [40]

Figure 7-24: Scheme of DSC

Subsequently, the sample is cooled at a defined cooling rate below the crystallite melting point. In the second melting constant product changes are detected. [36] To determine the heat of fusion, it is necessary to fully grasp the melting range. Accordingly, the limits of integration need to be established. [42]

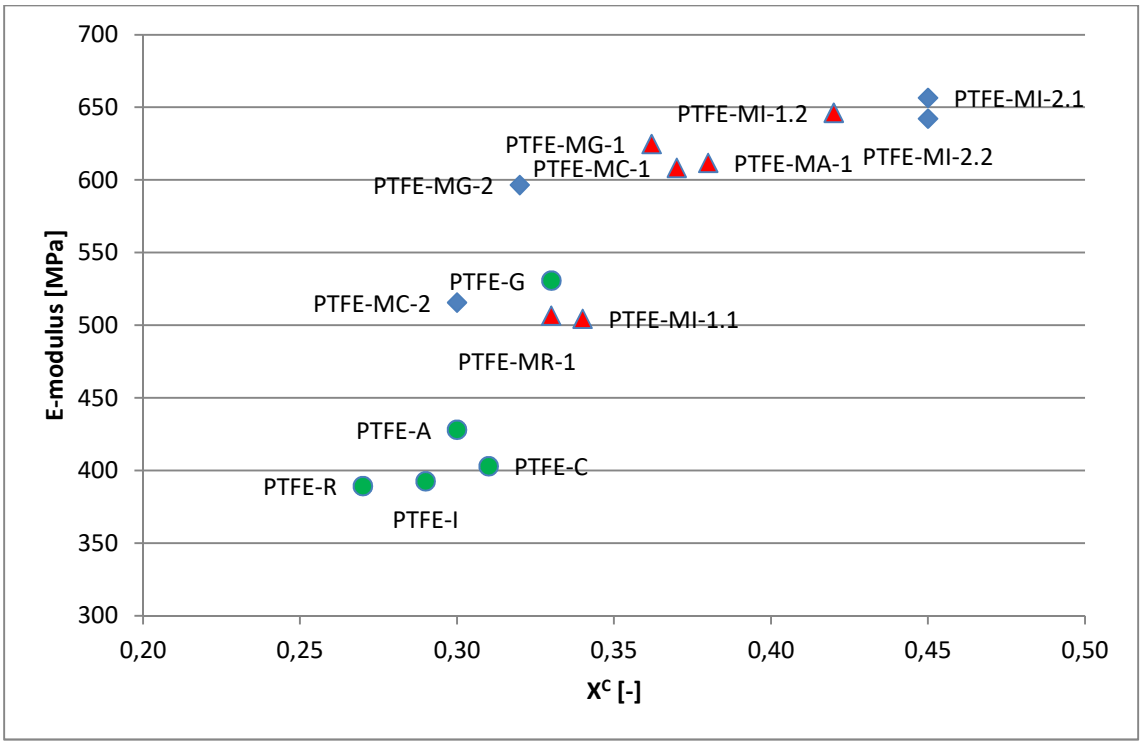


Figure 7-25: With increasing crystallinity the modulus of elasticity increases

As it is expected from semi-crystalline thermoplastics the crystalline fraction acts as a mechanical stabilizer when the polymer is set under tensile stress. Same is true for the PTFE-materials. As it can be seen in Figure 7-25 there is a strict correlation between an increasing crystallinity and an increasing modulus of elasticity. The spread as well for the crystalline fraction as for the E-modulus of the individual PTFE-grades is that high, that their analysis is a worthful tool for material identification. However if the crystallites tend for large diameter

they enhance cold flow of the material and thus are weakening the physical strength of the material.

7.6 Investigation of melting behaviour

A characteristic feature of the appearance of the DSC curves of Standard PTFE and modified PTFE are the broad melting peaks with a high crystalline melting point of about 329 °C and 326 °C respectively in the 1st heating. The width of the melting peak is an image of the crystallite size: small crystallites melt first, while large crystallites can follow only at higher temperatures. As table 7-4 shows further on, there is a systematic difference between 1st and 2nd heating. [43] The heat of fusion of the 2nd heating is lower than that of the 1st heating in a systematic way. This is because the cooling curve with a cooling rate of -1 °C per minute applied during the sintering of the specimen results in significantly slower recrystallization than is the case in the -10 °C/min. during the cooling under the DSC analysis of the case. As a consequence, the specimens show a significantly higher degree of crystallinity in the 1st heating than in the 2nd heating. At the same time the peak maxima of the 2nd heating move slightly towards lower temperatures compared to those of the 1st heating. This is a further indication of the reduction of degree of crystallinity as a result of rapid cooling during the DSC analysis. The melting and crystallization behaviour of PTFE changes with the addition of the comonomer PPVE. [48]

In general if the endothermic peak widens the melting temperature decreases. [44] PPVE as a modifier reduces the crystallinity in the case of modified PTFE types and thus compensates for the higher tendency to crystallize due to their lower molecular weights. As a consequence, the modified PTFE types exhibit enthalpies of fusion in principle more or less like those of Standard PTFE. However, in the majority of examples of products they are higher. After polymerization, both Standard PTFE and modified PTFE are highly crystalline and do not recrystallize perfectly after the first reflow. Reasons for this are the high molecular weights and the associated low chain mobility. [43]

Material	PPVE [wt%]	T_{m1} [°C]	ΔH_{f1} [J*g^{-1}]	X_{C0} [%]	T_{m2} [°C]	ΔH_{f2} [J*g^{-1}]	X_C [%]
PTFE-MG-1	0,10	326,1	29,7	36,2	323,6	25,1	30,6
PTFE-MG-2	0,05	325,9	26,4	32,2	324,0	23,2	28,3
PTFE-G	0,00	329,1	26,9	32,8	327,9	23,1	28,2
PTFE-MC-1	0,08	327,0	30,3	37,0	324,1	25,2	30,7
PTFE-MC-2	0,07	325,2	24,4	29,8	328,4	21,8	26,6
PTFE-C	0,00	328,4	25,3	30,9	328,0	23,2	28,3
PTFE-MA-1	0,08	327,2	31,2	38,0	324,3	26,4	32,2
PTFE-A	0,00	327,7	24,4	29,8	328	22,6	27,6
PTFE-MI-1.1	0,08	325,7	27,7	33,8	323,4	23,8	29,0
PTFE-MI-1.2	0,11	327,9	34,4	42,0	324,9	29,3	35,7
PTFE-MI-2.1	0,07	328,3	36,9	45,0	326	31,1	37,9
PTFE-MI-2.2	0,04	328,5	36,5	44,5	326,1	30,5	37,2
PTFE-I	0,00	328,6	23,6	28,8	327,8	21,5	26,2
PTFE-MR-1	0,07	325,4	27,4	33,4	323	23,5	28,7
PTFE-R	0,00	328,9	22,5	27,4	328,2	20,8	25,4

Table 7-4: Melting temperature, heat of fusion and crystallization of the samples at the 1st and 2nd heating

A lower melting peak is detected on average for the modified PTFE grades. This demonstrates that the PPVE interferes with the crystallization process, so that a small crystallite size is preferably formed. The narrow crystallite size in conjunction with the lower average size in the modified PTFE types also has optical consequences, which can be recognized by a comparatively higher level of transparency. [43] The low-modified grades have roughly the same crystallinity as the Standard ones. Apart from the PTFE-I material which resembles the other types of PTFE, the remaining PTFE-MI products have a highly increased crystallinity. As already mentioned this suggests a low molecular weight.

Also in the cooling process the PTFE-I types have a greater enthalpy for recrystallization, different from the other PTFE products, especially in comparison with the low-modified PTFE grades. The temperatures of recrystallization differ significantly between the modified grades, low- and high-modified, and Standard types. While the recrystallization under DSC conditions takes place at 312 °C – 311 °C in case of Standard PTFE types, this occurs first at 305 °C – 304 °C for modified PTFE types (Fig. 7-28). This is due to the crystallization of the modifiers PPVE which has a disturbing influence. The DSC analysis thus provides, in addition to the FT-IR method, the detection whether PTFE is present in its Standard or modified version.

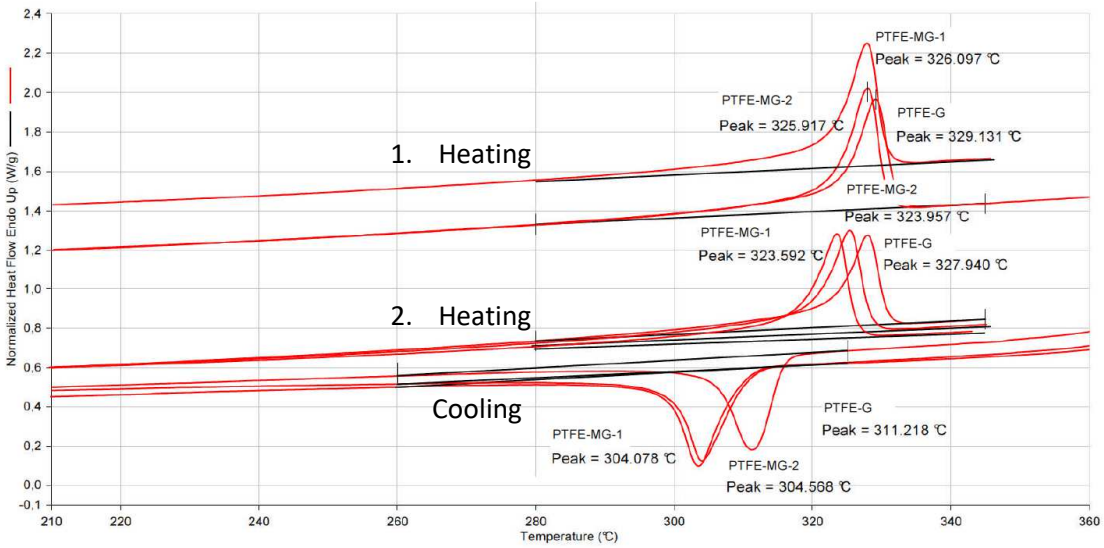


Figure 7-26: Results of the DSC analysis on the sample of PTFE-(M)G-materials

As an example, figure 7-26 above shows PTFE-MG-material curves and illustrates the differences in the different modified materials that have already been explained above. The upper curves show the behaviour at the 1st heating, the ones below the behaviour at the 2nd heating, and at the bottom are the results of recrystallization.

Additionally the example in figure 7-27 of PTFE-MR-1 shows an inhomogeneous modifier incorporation, which becomes clearly visible by the analysis of the peak of recrystallization.

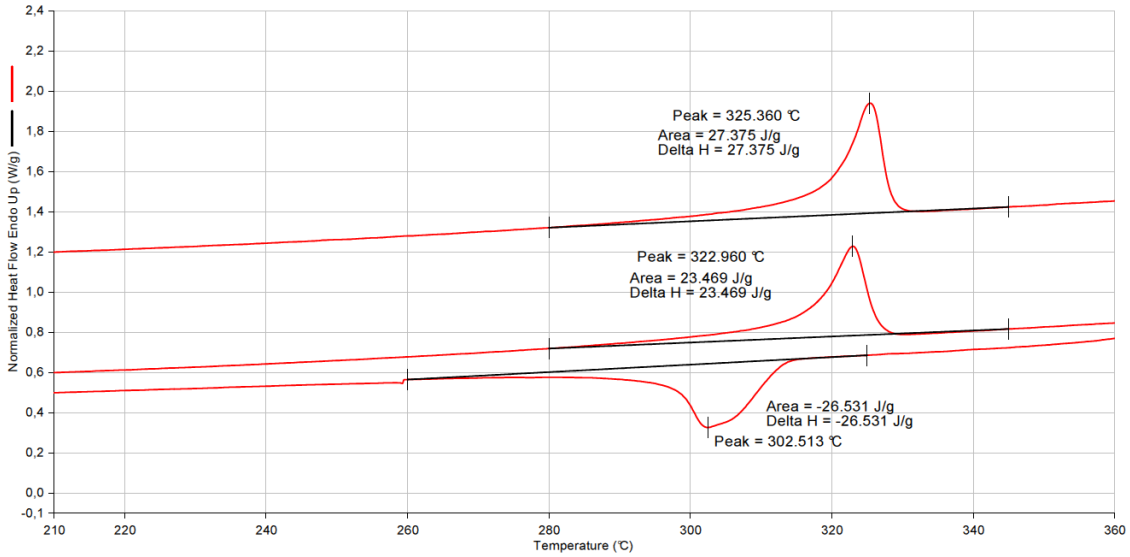


Figure 7-27: Results of the DSC analysis on the sample of PTFE-MR-1 material

All peaks describe the melting respectively the recrystallization transformation of the crystalline regions of the PTFE. When sintered under standard conditions, the degree of crystallinity of the PTFE is approximately 60 – 70 % while is in the range of 30-40% amorphous.

The glass transition temperature of PTFE is in the range of 140 °C – 145 °C and remains unconsidered in the tests carried out, as, due to the dominating crystalline fractions in contrast to the amorphous, it does not undergo any significant change at this point.

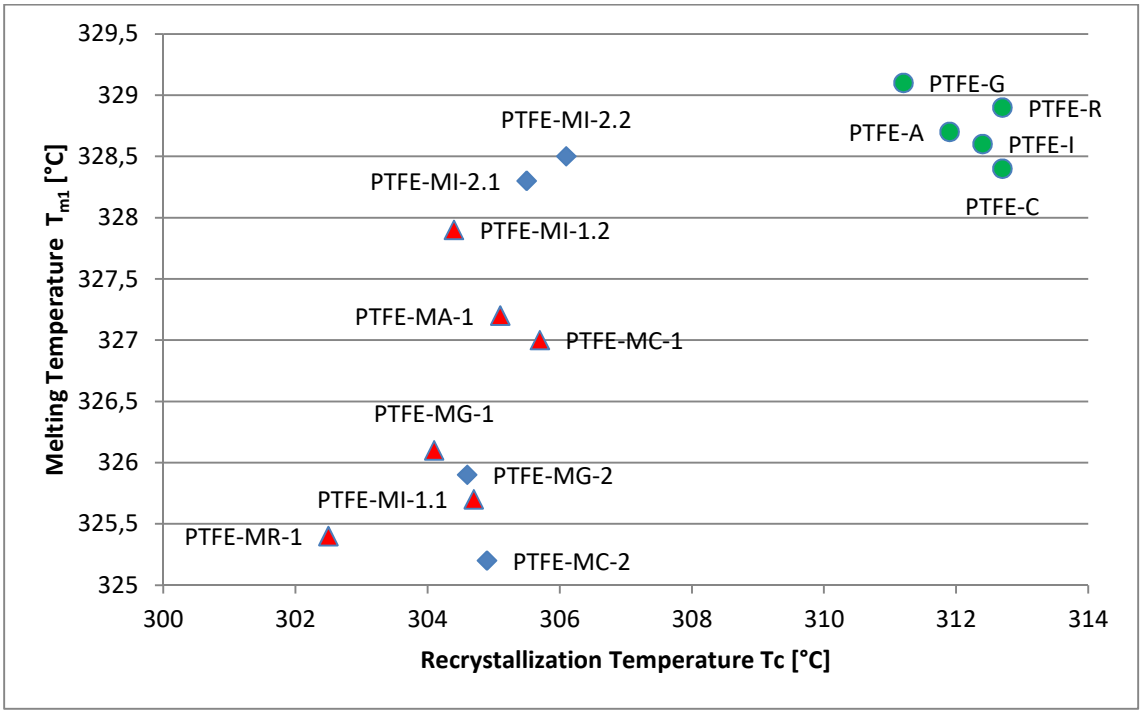


Figure 7-28: Overview of melting temperature and recrystallization temperature of all investigated PTFE-M products

Figure 7-28 above shows that the melting temperature and the recrystallization temperature significantly drop as a result of the disturbance of the crystallite structure caused by the incorporation of even relatively low amounts of the comonomer PPVE. The special position of all Standard PTFE types (marked green) is clearly visible.

The relationship between the melting temperature and the comonomer content for PPVE-modified PTFE polymers can be considered based on the theory of the melting behaviour of the co-polymer under the assumption that the PPVE units are completely excluded from the PTFE crystallites. According to the Flory-equation, lowering the equilibrium melting temperature for homopolymers having a random distribution of X-molar co-monomer fraction is defined as follows: [40]

$$\frac{1}{T0m(X)} - \frac{1}{T0m} = -\frac{R}{\Delta H0}\ln(1 - X) \qquad (7.4)$$

where T_{0m} (X) is the Equilibrium melting point

The dynamically measured melting temperatures were determined in this work instead of the equilibrium melting temperatures. In a first approximation they also follow the scheme of the Flory equation 7.4, as can be seen in figure 7-29.

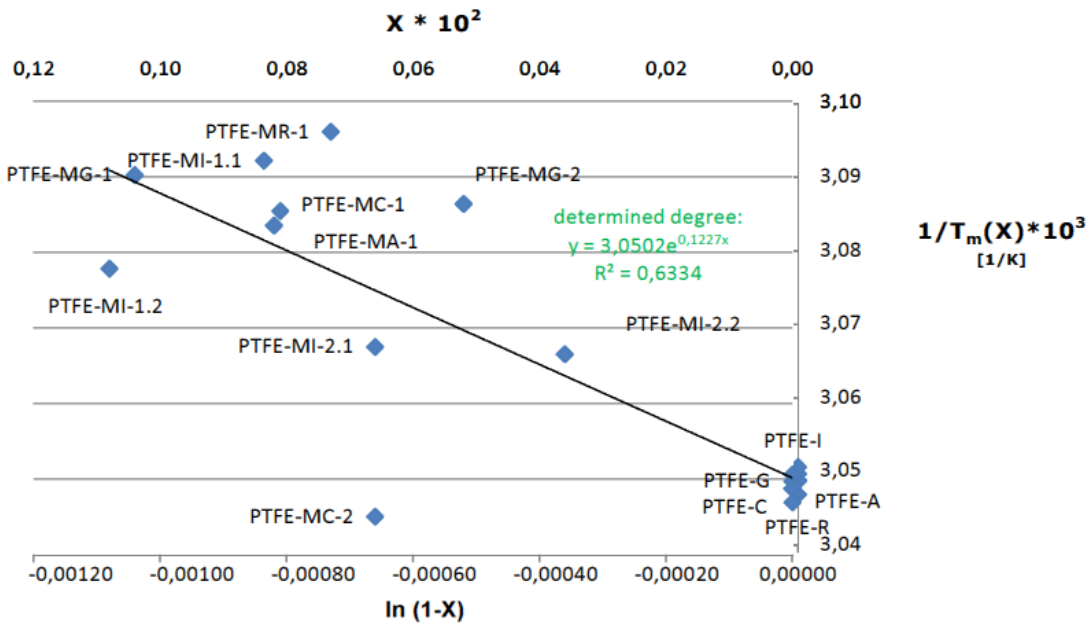


Figure 7-29: The reciprocal of the melting temperature of the investigated PTFE samples plotted against the mole fraction of the modifier content. Plotted is also the linear regression line of the determined melting temperatures (determined degree: $y = 3.0502e^{0.1227x}$, $R^2 = 0.6334$).

While the scattering range of all Standard grades of this study is very small, several candidates of the modified grades do not show a good fit to the regression line. Moreover, grades like PTFE-MC-2 do not even follow the rules of the Flory-equation. The origin of this deviation can be explained as follwos:

Flory describes the correlation between melting temperature and comonomer content. The polymer grades evaluated in this study do not only contain different quantities of comonomer, but also show significant differences in molecular weight and molecular weight distribution. The latter is true especially for PTFE-MC-2 which is polymerized with a very broad molecular weight. On top of this the statistical incorporation of PPVE into the polymer chain in amounts around 0.1 wt-% may generate segments within the polymer chain, containing no PPVE over one hundred monomer units of TFE and more. Thus, another assumption of the Flory theory, that no PPVE may be part of crystal lattices, could be infringed too. Taking all these aspects into consideration, the worse regression in figure 7-29 can be easily explained.

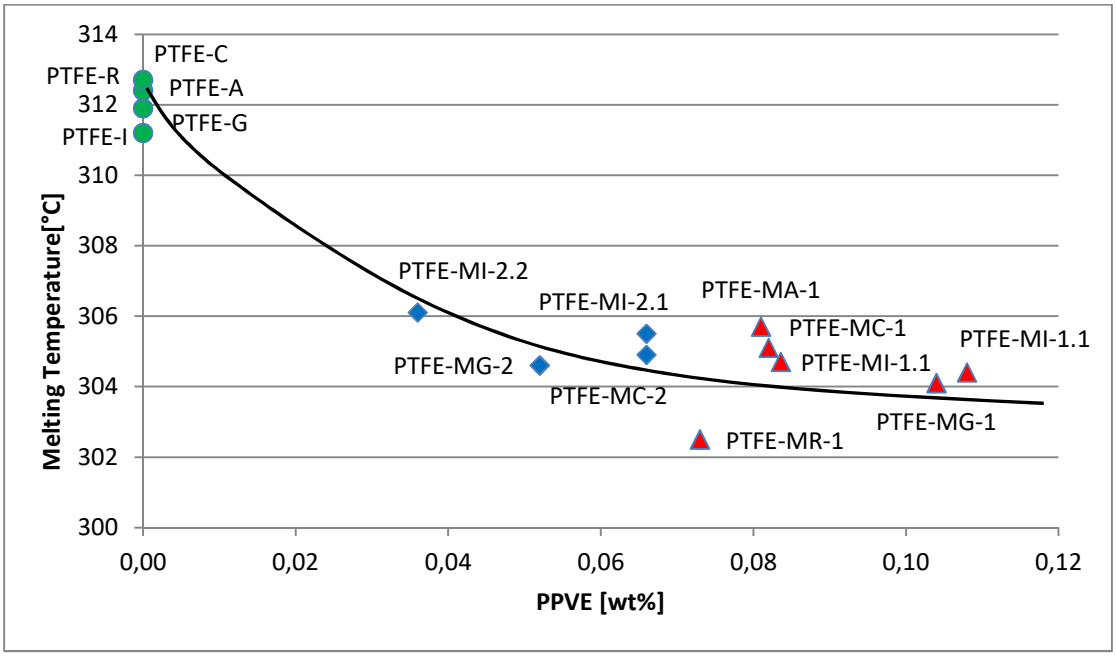


Figure 7-30: PPVE content and melting temperature (green - non modified, blue - modified low, red - highly modified)

As mentioned above, the decrease in the melting temperature is again linked to the PPVE content (Fig. 7-30). All modified PTFE types have a significantly reduced melting temperature. It is also clearly visible that even a very small PPVE content causes a significant reduction in melting temperature. This observation is caused by the fact that the smaller crystallites of the modified PTFE in DSC determination are melting earlier compared to the larger ones in rising temperatures. Further increases in PPVE content in the range of 0.04 - 0.12 wt%, however, have only a slight influence on the melting temperature. [48]

For product identification DSC-method can be considered as the most important tool, not only for product identification but also for failures in polymerization and in material processing. For the first time, now a clear DSC-picture for the most important PTFE-grades is available:

The incorporation of the comonomer PPVE in the molecular chain of PTFE disturbs the crystallization process, especially is reducing the size of the formed crystallites. Simultaneously the molecular weight has a strong impact on the part of the crystalline phase of the polymer in both modified and Standard materials. DSC measurement detects both

contributions by the means of melting temperature, temperature of recrystallization and enthalpy of phase transitions.

7.7 Dynamic Mechanical Analysis (DMA)

Various thermophysical and thermomechanical properties were measured from – 170°C to 370°C. The comparison of the different physical properties allows more detailed insight into the phase transistions during thermal treatment. For the test results it can be said that the phase changes from the ordered to the disordered structures have a significant impaction the material mechanical strength. The influences on the thermal expansion and the thermal transport properties are less strong but can be clearly seen as well. [45]

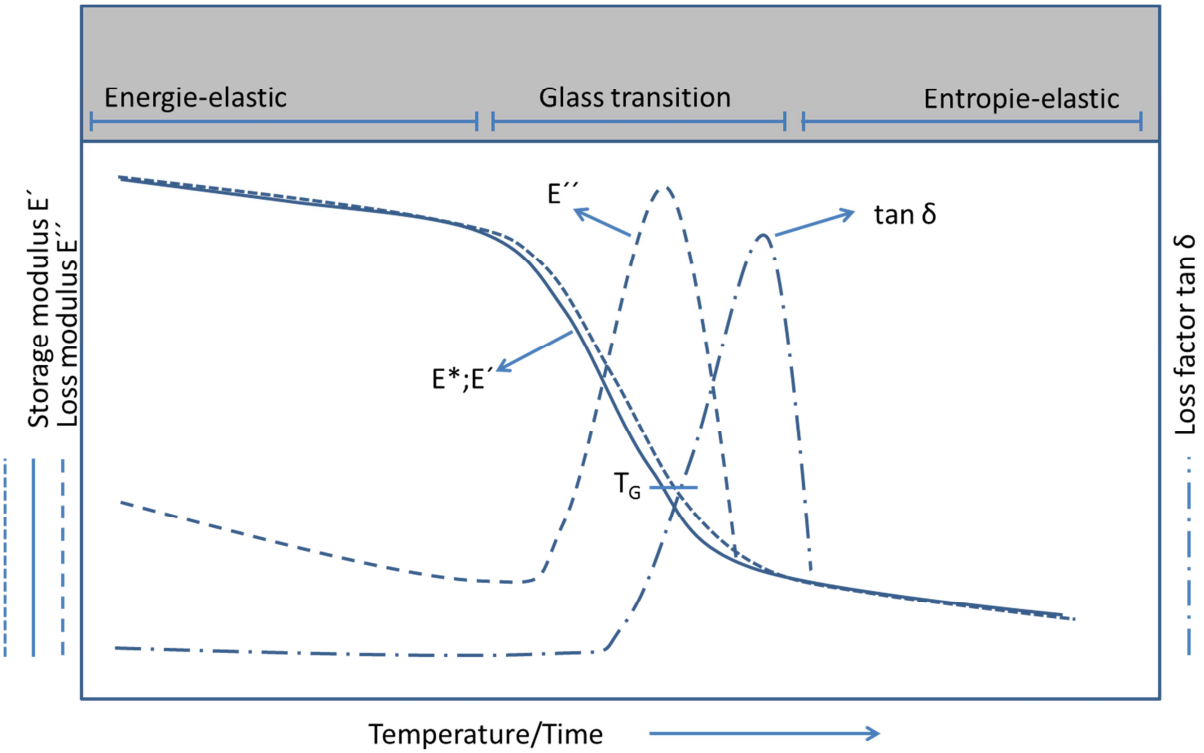


Figure 7-31: DMA of Complex modulus E*, Storage modulus E´, Loss modulus E´´ and Loss factor tan δ as a function of temperature for amorphous polymers [2]

In order to understand and to measure the complex material behaviour of PTFE, the modulus of elasticity must be subject to special consideration. As already mentioned, the materials are offering both viscous and elastic behaviours. Modulus of elasticity thus has an elastic portion, the storage modulus E', and a viscous component, the loss modulus E". [46]

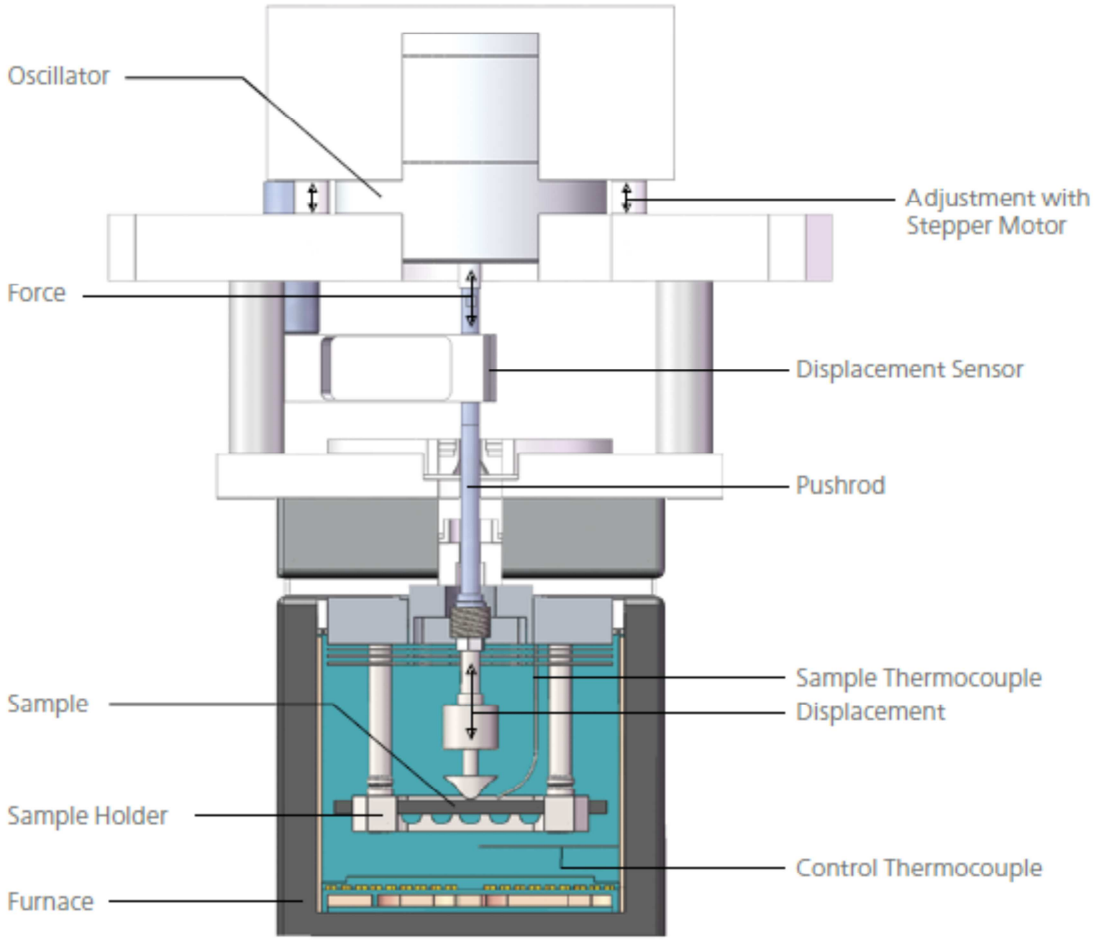


Figure 7-32: Functional principle of DMA [38]

By applying a sinusoidal deformation to a sample of known geometry DMA works. The material sample is subjected by a controlled stress and strain. The sample will then deform a certain amount for a known stress. The stiffness determined the degree of deforming. To generate the sinusoidal wave a force motor is used and this is transmitted to the sample via a drive shaft. [38]

The loss factor tan δ (=E´´/E`) is the ratio of the loss modulus and the storage modulus and is a signal for the damping characteristics. As can be seen in the figures below in the curve of tan δ the softenings (glass transitions) are to be as peaks. [47] Apart from the determination of the amount of rigidity, the effects of temperature and strain rate on the viscoelastic material behaviour can be characterized.

The DMA analysis is often measured across several frequencies in order to detect a frequency dependency. Within this thesis, measurements were taken at frequencies of 0.5 Hz, 1.0 Hz, 2.5 Hz and 10 Hz. A frequency dependency is detected in the dynamic mechanical data of the viscoelastic areas, that is, the higher the frequency, the higher the tan δ-maximum. Furthermore, with increasing frequency the relaxation transitions move towards higher temperatures.

In general, in the examined PTFE materials the complex modulus and the storage modulus below the glass transition temperature are relatively high. This can be explained by the very low mobility of the molecular segments.

The behaviour of the material is almost pure elastic, due to the low loading condition and the loss modulus therefore is very low. This suggests that the loss factor is also small. By heating up the specimen a first change can be observed in the temperature range of 30 °C – 35 °C and then again upon reaching the glass transition temperature in the range of 125 °C – 140 °C.

In these transition areas, the intermolecular attraction forces are so weak that a significant increase in polymer chain mobility takes place, causing a great material softening. As can be seen in the figures below, this causes a strong decrease in E * and E' (storage modulus) and simultaneously an increase of E" (loss modulus) and tan δ (loss factor). Under further influence of temperature, E' (storage modulus) and E" (loss modulus) decrease with increasing temperature because the very high molecular mobility leads to a progressive softening.

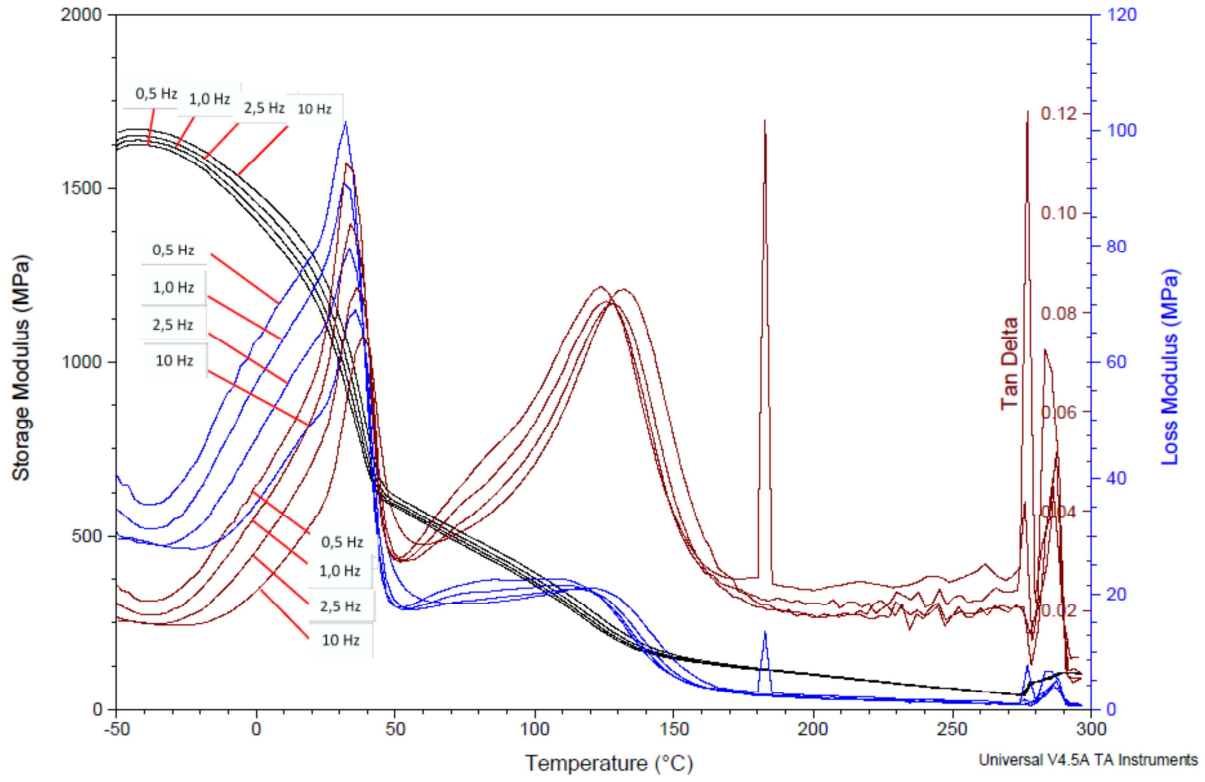


Figure 7-33: Summary of the DMA measurements at 0.5 Hz, 1.0 Hz, 2.5 Hz and 10 Hz for PTFE-MG-1

The cold flow increases at higher temperatures. At 30°C – 35°C there is a strong decrease. At 180°C there is a measurement artefact, which has no influence and must not be respected.

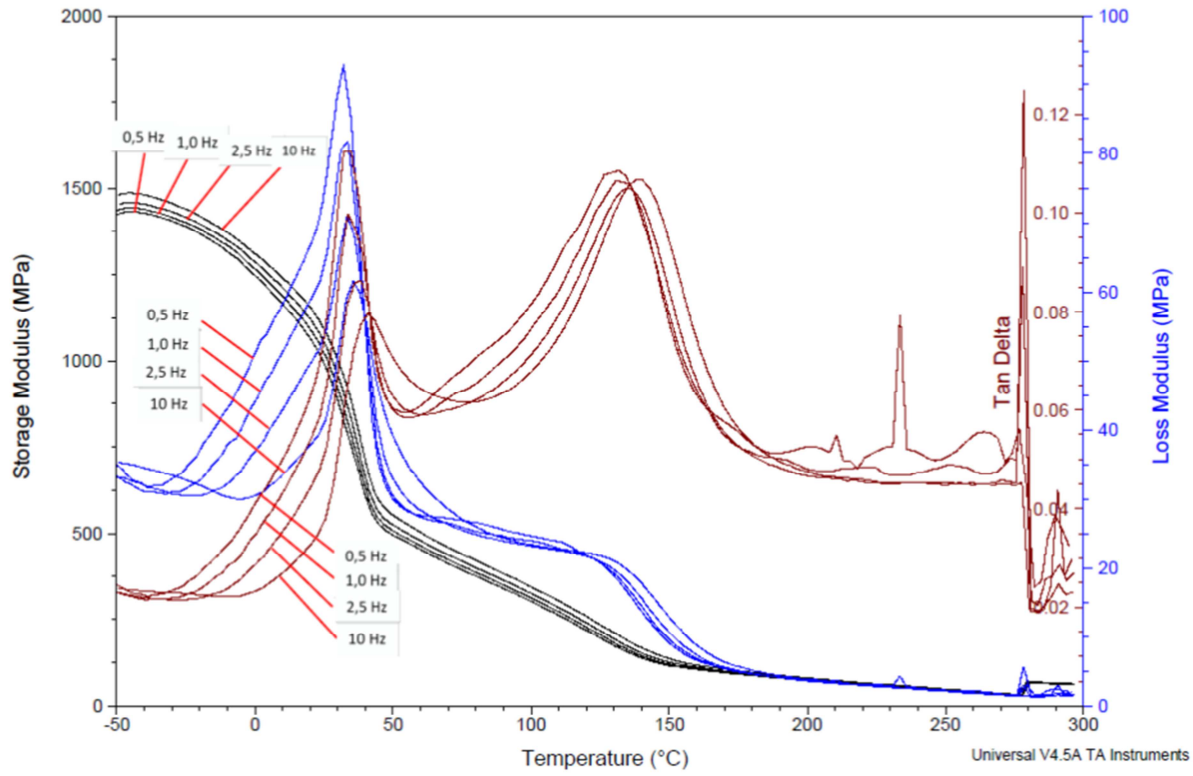


Figure 7-34: Summary of the DMA measurements at 0.5 Hz, 1.0 Hz, 2.5 Hz and 10 Hz for PTFE-G

As seen above in figure 7-34, measurements at frequencies of 0.5 Hz, 1.0 Hz, 2.5 Hz and 10 Hz (left to right respectively downwards) were performed. The differences in values between figure 7-33 (modified PTFE) and figure 7-34 (Standard PTFE) can be seen in table 7-5. At the beginning of the measurement the loss modulus in these areas is still relatively low, which means that the material responds more like a solid body and the mechanical energy stored during deformation suffers virtually no loss and is discharged back. The comparison clarifies that the lower the test frequency, the more the increase of loss modulus and tan δ begins in the first conversion at 30 °C – 35 °C. From this area the material is losing its elastic properties more and more and by the strain placed on the system mechanical energy is converted to a larger share into heat energy (increasing loss modulus). The storage modulus decreases and tan δ achieves a second maximum in the area of the glass transition at 125 °C – 140 °C. Subsequently, the loss modulus is reduced further on, to finally reach its minimum.

The frequency-induced shift of the peak maxima of loss modulus and tan δ of the two materials PTFE MG-1 and PTFE-G is shown in the following table 7-5 and can be seen in figure 7-35:

	PTFE-MG-1	PTFE-MG-1	PTFE-G	PTFE-G
Frequenz (Hz)	T by loss modulus (°C)	T by loss factor (°C)	T by loss modulus (°C)	T by loss factor (°C)
0,5	32,45	32,45	32,07	32,61
1	31,26	33,95	33,68	33,68
2,5	33,68	36,1	33,41	38,25
10	35,83	38,25	35,57	40,94

Table 7-5: Temperature increase of the peak maxima of loss modulus and tan δ as a function of the measuring frequency

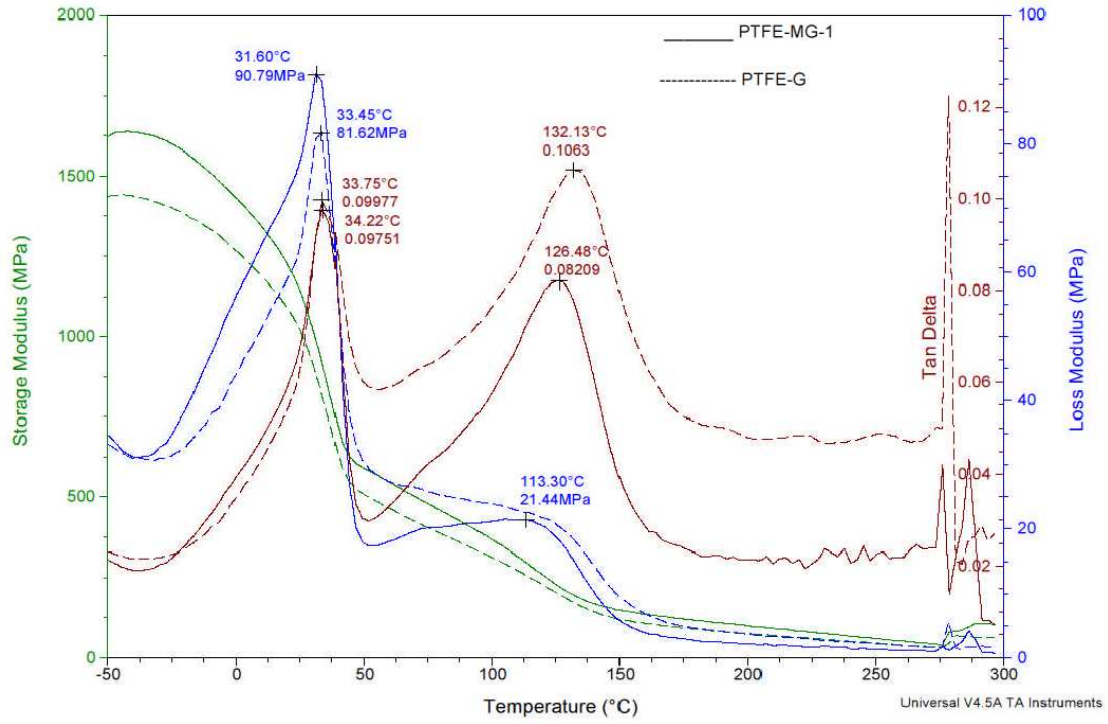


Figure 7-35: Comparison of modified and Standard PTFE material (PTFE-MG-1and PTFE-G) at 2.5 Hz

Storage modulus E':
Across the entire temperature range of -50 °C – 250 °C modified PTFE has the higher storage modulus. It can thus absorb more energy under load and release it again when the load is taken away.

Loss modulus E"
In the area of the first conversion at about 30 °C - 35 °C modified and Standard PTFE show a comparable behaviour. After exceeding this range and up to α-relaxation at 125 °C - 140 °C the loss modulus of modified PTFE first drops significantly, in order to then rise continuously. For Standard PTFE the decrease in the loss modulus after passing through the first conversion is initially much less pronounced, but then falls further subsequent to the α-relaxation.

As a consequence of this different behaviour of loss modulus, the storage moduli of modified and Standard PTFE continue to approach between the first conversion and α-relaxation. The property advantage of modified PTFE, which is particularly pronounced at lower

temperatures, thus is partially lost. The measurements in this study were done at 23°C to analyze the mechanical differences. If these differences are compared with the findings in DMA, especially considering the different levels of storage moduli for Standard and modified PTFE it clearly can be stated, that both methods of product characterization come to a similar conclusion.

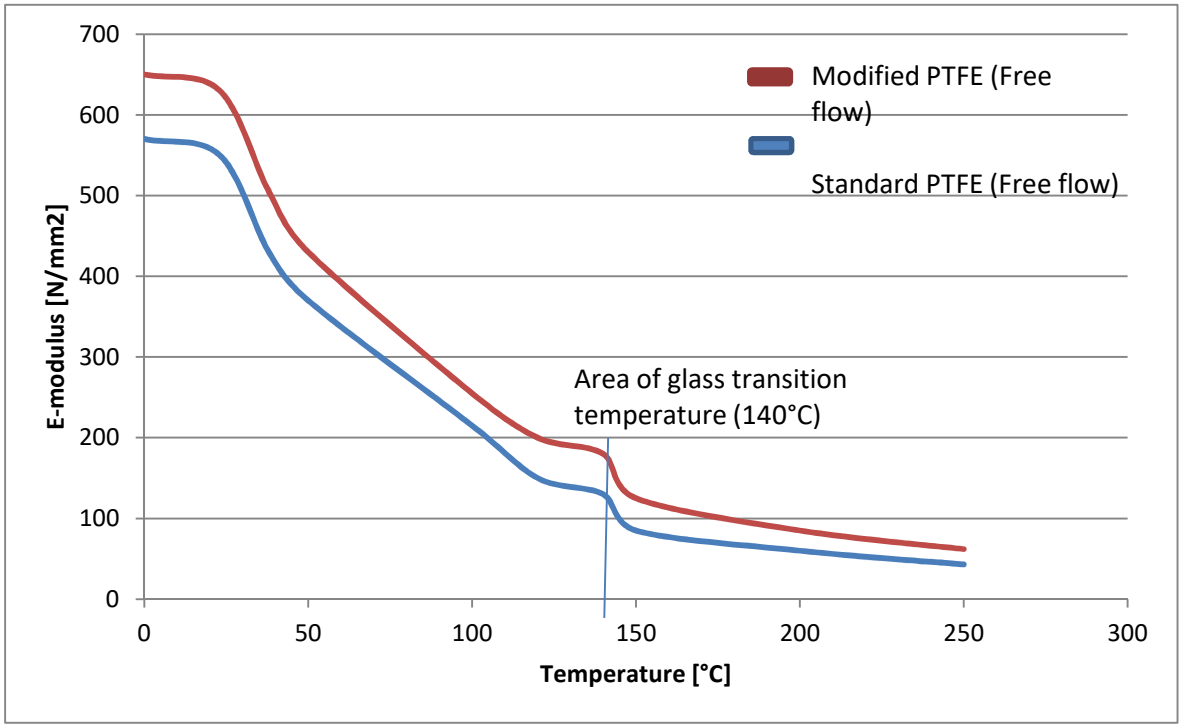


Figure 7-36: E-modulus as a function of temperature

As an example, figure 7-36 above shows the E-modulus as a function of temperature for free flow Standard and modified PTFE material. With increasing temperature the E-modulus is decreasing. The buckling at about 140°C is the area of glass transition temperature.

Loss factor tan δ:

The curves of tan δ are almost identical in the region of the first conversion. Subsequently tan δ for Standard PTFE shows significantly higher values than for modified PTFE. This means that for Standard PTFE, the storage modulus E' plays a much larger role in this temperature range than the loss modulus E" - a fact that clearly accounts for the known cold flow of Standard PTFE. The DMA is a method for the characterization of dynamic properties of polymers, which are important for products like bellows and membranes. Product characterizations with permanent or slowly changing strains provide important informations for static loaded products, especially for long-term applications. Static strains provide important values for the cold flow. This means, that only the evaluation of all mechanical and physical measurement results give a clear view on the different material characteristics.

7.8 Interpretation of results

It is well known since many years that the processing of PTFE is very critical and sensitive depending on the processing parameters. Besides the extreme resistance against any kind of solvent and the low friction coefficient it is also well known that PTFE shows a high deformation rate under compression load, the so called “cold flow” which is limiting the application in sealing- and wear- systems.

Since a number of years there are developments ongoing to modify PTFE basic materials by changing the molecular weight and by using fluorinated co-monomers. Those modifications are influencing the material characteristics significantly. By different methods like DSC- and DMA- analysis the influence of the modifiers could be shown clearly on the thermal as well as on the mechanical behaviour. By investigating the influences of molecular weight, molecular weight distribution and modifier content systematically of a total of 15 different grades, for the first time the worldwide mostly-known PTFE-materials, with individually balanced modifier contents and molecular weights, were analyzed. As a result a clear fingerprint for each material and its position in a global PTFE roadmap over the broad range of mainly modified PTFE could be identified and described. It turned out that it is not as simple as just grouping the materials on one side in Standard, low- and high- modified and on the other side in high-, medium- and low-molecular weight categories. Furthermore it clearly becomes visible that additional factors such as the distribution of the molecular weight itself and the kind of modifier incorporation must be taken into consideration in order to completely understand the materials in processing and its final property profile.

Those results discussed in this study are offering for the first time a clear picture on the modifying possibilities and the balancing of molecular weight and modifier content. Further results – especially discussing the wear behaviour and the “cold flow” will be shown and discussed in following chapters.

7.8.1 Concept for developing a PTFE roadmap

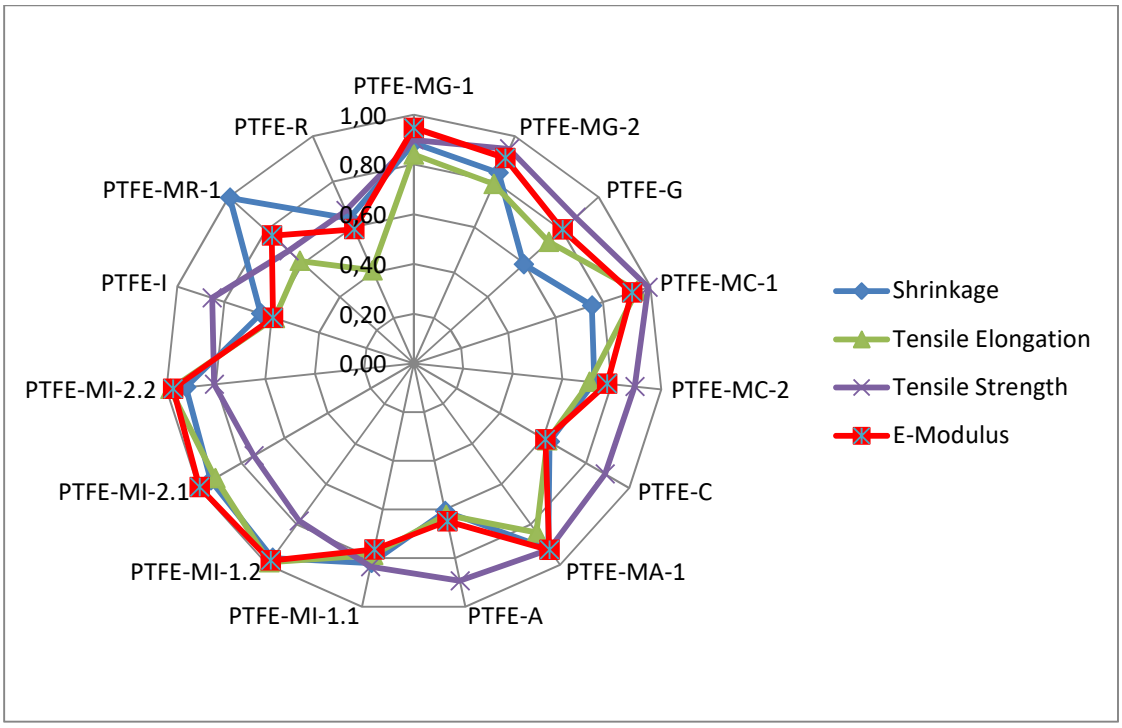


Figure 7-37: Network/Concept for PTFE roadmap

The concept in figure 7-37 is a guideline for the characterized materials to indicate the differences in mechanical and physical properties. Aside from the important parameters like the molecular weight and particle size and their distribution this concept can be used to choose materials for different applications. For example for tensile elongation the PTFE-R material has an outstanding position in a disadvantegous way, while except of the PTFE-MR-1 all modified materials have better measurement results than the Standard materials, as expected. It is also remarkable that all PTFE-I materials have reduced tensile strength in relation to other materials, except, as already mentioned, of PTFE-R. But in contrast to this the modified PTFE-I materials have excellent E-moduli and good tensile elongations.

7.8.2 Selection of best Standard and modified PTFE

For the following chapters one Standard and one modified PTFE material are selected after all measurement results are evaluated. As a result for Standard material PTFE-G is choosen and for modified PTFE-MG-1 to discuss the way how characteristics are estimated (Fig. 7-38).

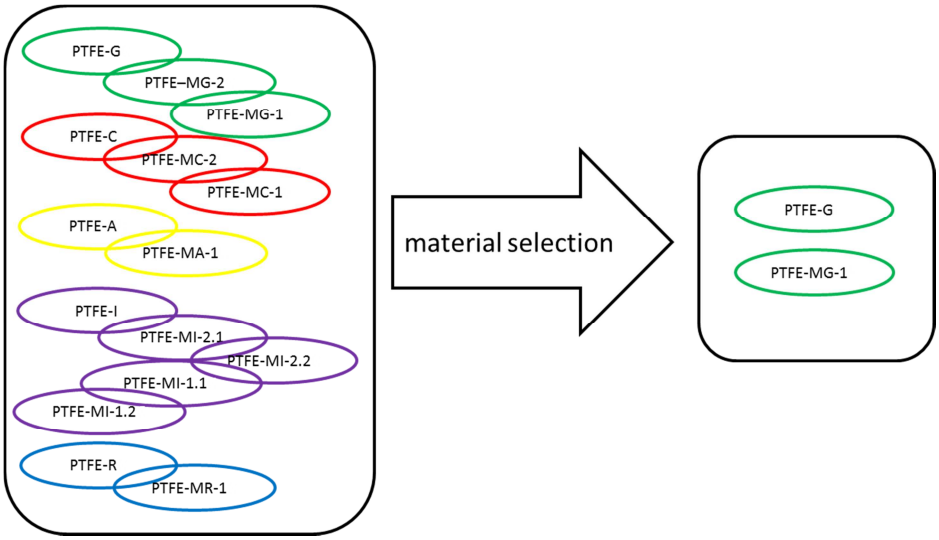


Figure 7-38: Material selection of best Standard and modified PTFE

These materials were selected under consideration of the results of all measurements mentioned above. As a conclusion they represent the best fit out of all properties. The selected Standard and modified PTFE materials will be blended with fillers and determined regarding physical and tribological characterization in the next chapters.

8 Impact of processing technology – Determination of the impact of moulding and sintering conditions on finished products

The physical and mechanical properties of polytetrafluoroethylene (PTFE) are influenced significantly by the processing conditions. Due to its high molecular weight, PTFE, although a thermoplastic material, is not melt-processable due to the high viscosity in the melting phase. Instead of injection moulding and extrusion, moulding by hydraulic presses and sintering are the techniques of choice to convert the PTFE from its powder state into finished particles. Both, the moulding and the sintering step play an import role for the property profile of the finished material. For Suspension-PTFE (S-PTFE) through moulding the air between the particles will mainly be removed. In case of agglomerated products, they are de-agglomerated und the contact between the surface of the primary particles is built up. Different powder properties of PTFE, such as low flow and free flow, significantly influence the required processing conditions. Final particle fusion at the outer circumference of the primary particles is the task of the sintering step. The crystalline-amorphous structure, and consequently also the property profile, is decisively determined by the cooling speed when passing the temperature of recrystallization of PTFE.

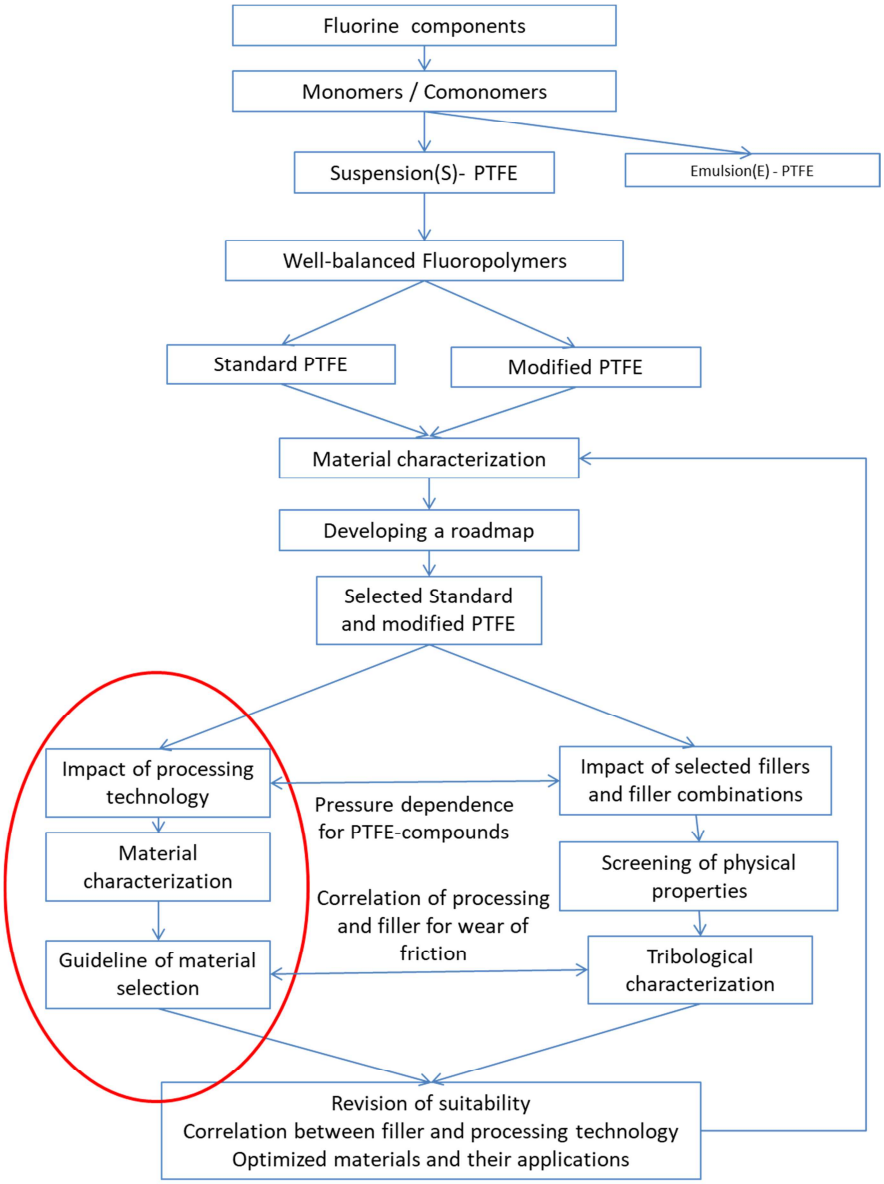


Figure 8-1: Overview of the systematic approach for optimization

8.1 Processing steps

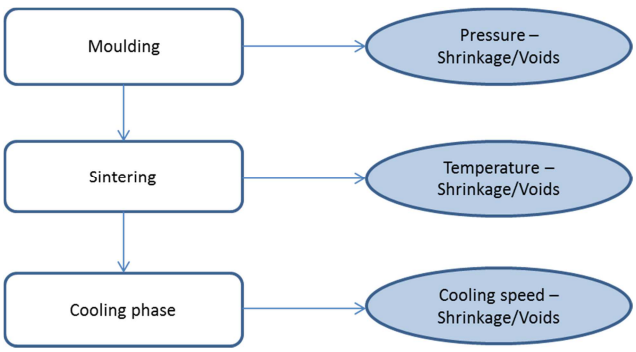


Figure 8-2: Processing steps

Moulding

A structural element built by PTFE powder is moulded at room temperature (23°C +/- 2 °C) with a defined pressure. Normally the maximum pressure depends on the consistence of the powder, low flow (non free flow) powder requires about 15 MPa moulding pressure, whereas free flow powder requires 25 - 35 MPa. The reason for this pressure difference is the need to open up the agglomerates in the free flow powders. The process of moulding should be run slowly and smoothly without any interruption in order to enable the entrapped air to be released and the powder particles to build up effective surface contact. After reaching the maximum pressure, it must be held (so-called pressure dwell time) in order to enable the particles by flow processes in their crystalline regions to adjust shape and built up contact areas within the particles. The moulding process is kept constant in this study for this product, but in general this process can be modified for other products and others targeted applications (Fig.6-6). Altough the processing conditions are constant, a general scientific declaration can be made and general rules are discussed here.

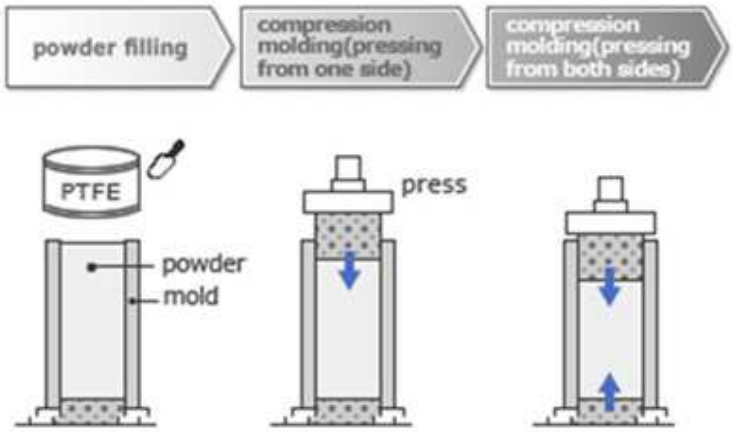


Figure 8-3: Moulding process [41]

By the flowing of particles internal stress is reduced and material inconsistencies are eliminated. Homogenious pressure propagation between the particles is the parameter which determines the duration of the dwell time. The initial phase of pressure decay must be performed under controlled conditions in order to avoid crack formation by billet snap back, because of the existing relaxation behaviour of moulded PTFE and the resilience of entrapped air in the billet. In order to enable the outgassing of entrapped air respectively stress-relaxation, after pressure released and demoulding the preform is stored for some time without stress at ambient temperature. The uniform moulding and the stress relaxation is getting more and more important especially for a bigger mould. [36]

Sintering

After moulding, the preform must be treated by a defined sintering cycle. It is starting with a defined heating ramp up to a maximum temperature of 370 - 380°C. In this study different maximum sinter temperatures have been taken into account to control the impact on the

material properties. PTFE is converted into an amorphous melt above the crystalline melting point, which is positioned at around 342°C for non-sintered PTFE. Particle fusion is the consequence of this heat treatment leading to a compact polymer structure. The sintering cycle is performed in controlled sinter ovens by using air circulation for heat transfer. For bigger parts it is recommended that the melting temperature range is passed with applying low temperature ramp because volume is increasing and generates stress. Although the melting temperature is exceeded, the sintering of the moulds occur „mould-free“, the parts keep its shape due to the very high gel stability as a consequence of the high molecular weight of PTFE. [36]

Cooling phase

The cooling phase after reaching the maximum sintering temperature is exactly defined by the highest thickness and in most cases very slow. Especially the range between the maximum sinter temperature and 260°C is very important to be run slowly and very controlled depending on thickness of structure. When the moulded structure reaches the temperature of recrystallisation it shrinks depending on the cooling rate/degree of crystallinity, which is the origin of stress. Minimizing the temperature differences within the mould by slow cooling rate is recommended, because the more uniform the mould is cooled, the lower the resulting stress. Minimizing internal stress helps to reduce the probability of crack formation. After the completion of the cooling phase machining processes like skiving, drilling and shaping are typically applied to manufacture the final parts. [36]

8.2 Process characterization – influence of free flow and low flow material

For this work four different materials were chosen for the polymer processing studies, two low flow (non free flow) materials prepared by modified and Standard PTFE and two free flow materials based on modified and Standard PTFE. Finally S-PTFE is called low flow or standard-flow, because at the end of the polymerization process the particle size is about 25µm and shows a ragged grain surface (see Fig. 8-4 a and b). This low flow powder is also the basic product for the agglomeration product, defined as free flow material. As already described earlier the low flow material is agglomerated to free flow material to a particle size of about 200 – 500µm and after that separated und dried. [7]

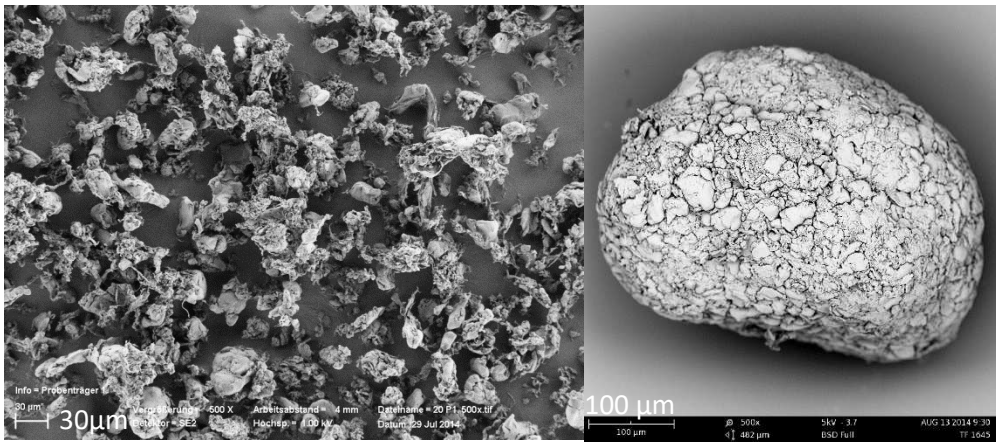


Figure 8-4: a) Low flow and b) Free flow S-PTFE material [7]

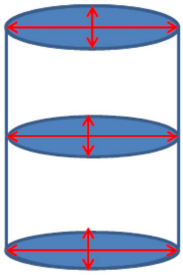
For preparing the test specimen by machining, hollow cylinders with ID = 40 mm and OD = 75 mm are used. The height is approximately 80 mm. In order to determine the impact of the processing parameter on the final material properties, the four materials (PTFE-LF-G, PTFE-LF-MG1, PTFE-FF-G and PTFE-FF-MG1) are used to mould and sinter the billets. The test specimen itself, e.g. for determining tensile strength and elongation, are prepared by machining it out of billets. Out of these billets 1,0 mm tape is skived and specimens are stamped out. Variations of the following parameters were applied:

- Moulding pressure
- Maximum sintering temperature
- Cooling rate

8.2.1 Processing conditions

Moulding pressure and moulding dwell time

For the study of the impact of the moulding conditions on the property profile of the finished product tests of each 5 billets of Ø 75/40 x 80 mm were needed from the materials PTFE-LF-G (Low flow), PTFE-LF-MG1 (Low flow), PTFE-FF-G (Free flow) and PTFE-FF-MG1 (Free Flow). The pressure dwell time is 5 min and the test specimens with a thickness of 1mm for determination of the tensile properties are punched out of skived film from the outer scope of a hollow cylinder. Visual inspection is performed at films of 0,1mm thickness for completion of particle fusion. While modifications of the moulding conditions are made, the sinter program is kept constant, based on experience. For the determination of the shrinkage the measurements are made at three positions of the billet: top, middle and bottom with displacement of 90°, see the movement in figure 8-5 below. Shrinkage may depend on the position of the billet and therefore shrinkage is measured at three different positions followed by calculating the average values, if possible.



Measurements:
top, middle, bottom – 90° displaced

Figure 8-5: Shrinkage measurements at plain cylinder Ø 60 mm

Moulding pressure [MPa]		Evaluations				
Low flow PTFE-LF-G PTFE-LF-MG1	Free flow PTFE-FF-G PTFE-FF-MG1	Tensile Strength	Tensile Elongation	Standard specific gravity (SSG)	Shrinkage	Visual inspection
5 10 15 20 25	20 25 30 35 40 45	For test specimens – skived film of 1mm out of hollow cylinder Ø75/40mm	For test specimens – skived film of 1mm out of hollow cylinder Ø75/40mm	Measurements at SSG-tablet	Measurements at plain cylinder Ø 60 mm	Skived film of 0,1mm out of plain cylinder Ø 60 mm
Maximum sinter temperature [°C]		Evaluations				
Low flow PTFE-LF-G PTFE-LF-MG1	Tensile Strength	Tensile Elongation	SSG	Shrinkage	Visual inspection	DSC
350 370 390 410 (only DSC) 430 (only DSC)	For test specimens – skived film of 1mm out of hollow cylinder Ø75/40mm	For test specimens – skived film of 1mm out of hollow cylinder Ø75/40mm	Measurements at SSG-tablet	Measurements at plain cylinder Ø 60 mm	Skived film of 0,1 mm out of plain cylinder Ø 60 mm	Test specimens stamped out of 1mm skived film

Table 8-1: Test matrix

The impact of very high sinter temperatures, even higher than the recommended temperatures onto the decay of the material properties is tested by using only low flow materials. This concept was choosen as the thermal stability of fluoropolymers only depends on its molecular composition, but not on the shape of the particles. As agglomeration of the polymers could bring additional impacts onto the temperature – effect correlation, the mostly simple system, the low flow version was used.

Sinter temperature and cooling

For the evaluation of determining the impact of different sinter conditions on the finished products, tests of each 5 cylinders with diameter 50 and height of 60 mm were used. The materials selected for these tests are PTFE-LF-G (Low flow) and PTFE-LF-MG1 (Low flow). While sinter conditions were changed, the moulding conditions have been kept constant:

- Moulding pressure: 15 MPa
- Moulding dwell time: 5 min (based on extended research study of polymer producers, for homogenious pressure distribution inside the billet a moulding dwell time of 1 – 1.5 minutes per centimeter of billet height is recommended [18])
- Pressure release: slow speed - pressure decay the first 30% within 3 sec. minimum, after that constant release until ejection

Sinter programs are applied with different maximum sinter temperatures of 350°C, 370°C and 390 °C. All following procedures are the same as described under chapter 7 with same ramps (± °C / minute) for heating up and cooling down. The temperature of recrystallization for PTFE is about 312 - 314 °C, for modified PTFE 306 - 308°C. [7]

To measure the degree of crystallinity the standard machine settings for differential scanning calorimetry (DSC) are as follows:

1) Heat from 150.00°C to 370.00°C at 10.00°C/min
2) Hold for 1.0 min at 370.00°C
3) Cool from 370.00°C to 150.00°C at 10.00°C/min
4) Hold for 2.0 min at 150.00°C
5) Heat from 150.00°C to 370.00°C at 10.00°C/min

The materials are the same as already described in this chapter. The evaluation for determining the impact of cooling speed DSC was performed using the following special settings:

As a variation of the standard settings, additionally the cooling speed from 370°C to 150°C was varied with either 10°C/min, 5°C/min or 1°C/min for PTFE-LF-MG1 and PTFE-LF-G in order to find the exact composition with regard to amorphous region and crystallinity for each material, depending on the cooling rate.

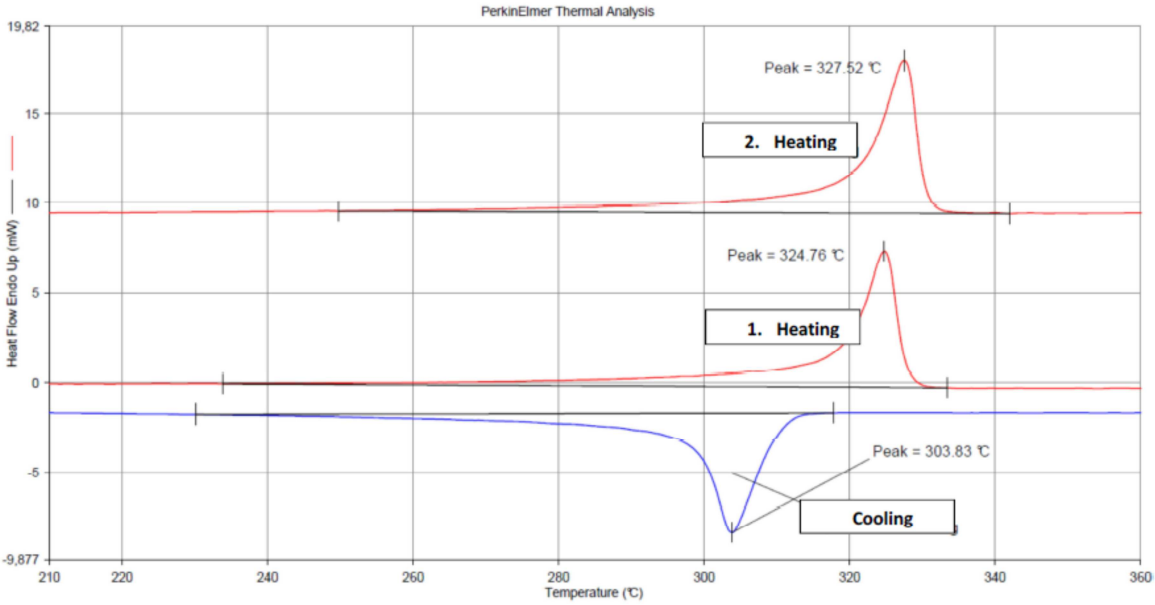


Figure 8-6: DSC-result for PTFE-LF-MG1 moulded with 15 MPa and sintered at maximum temperature of 375 °C

		Evaluations				
Materiale	**Pressure (MPa)**	**Maximum sinter temperature (°C)**	**Tensile Strength [MPa]**	**Tensile Elongation [%]**	**SSG [g/cm³]**	**Shrinkage [%]**
PTFE-LF-G	5	375	32,96	382,32	2,094	11,30
	10	375	34,03	395,38	2,159	9,13
	15	375	35,4	406,08	2,16	5,67
	20	375	35,15	393,18	2,159	4,23
	25	375	34,94	397,04	2,159	3,19
	15	350	32,05	346,04	2,155	4,79
	15	370	38,77	384,29	2,16	5,50
	15	390	36,79	433,91	2,164	5,66
PTFE-LF-MG1	5	375	35,59	454,14	2,15	12,96
	10	375	35,39	433,30	2,157	9,50
	15	375	37,56	467,24	2,159	6,65
	20	375	36,98	472,08	2,158	5,51
	25	375	35,7	431,78	2,157	4,86
	15	350	36,79	425,33	2,159	6,55
	15	370	34,22	422,87	2,159	6,67
	15	390	36,36	472,39	2,16	6,96
PTFE-FF-MG1	20	375	34,89	408,59	2,153	5,04
	25	375	34,19	397,11	2,157	4,44
	30	375	37,44	418,58	2,157	3,57
	35	375	38,67	439,81	2,156	3,64
	40	375	36,4	430,07	2,16	3,23
	45	375	37,21	443,12	2,158	3,57
PTFE-FF-G	20	375	33,08	351,97	2,154	3,49
	25	375	32,5	348,94	2,154	2,75
	30	375	34,07	358,13	2,154	2,55
	35	375	34,31	350,38	2,159	1,95
	40	375	34,85	363,96	2,154	1,88
	45	375	34,15	361,31	2,154	1,81

Table 8-2: Overview of all materials and test results (except DSC and visual inspection) – best results marked green

8.2.2 Analysis of tensile properties

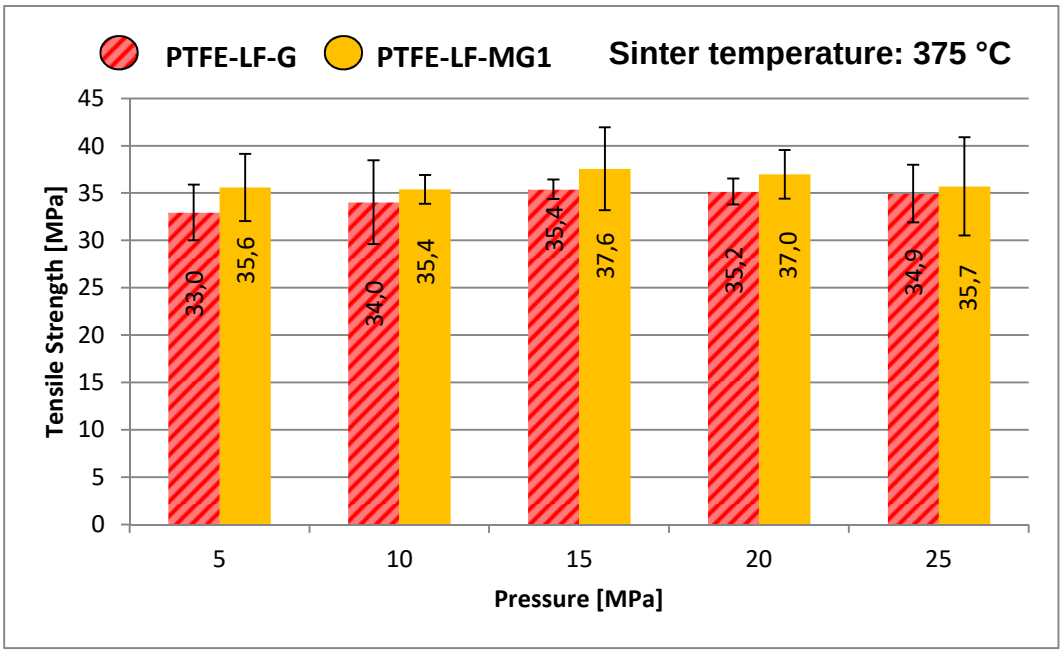


Figure 8-7: Impact of moulding pressure on tensile strength of PTFE-LF-G and PTFE-LF-MG1

As expected tensile strength as a function of the moulding pressure is higher for modified PTFE in relation to Standard PTFE (Fig. 8-7). But both materials show the best results at 15 MPa, which is the recommended standard moulding pressure for PTFE. Lower moulding pressure generates worse results, whereas the materials are not sensitive in relation to higher pressure within the applied pressure range. It further can be observed that the scattering range for PTFE-LF-G is more narrow than for PTFE-LF-MG1. The origin of this difference is the higher absolute value for elongation at break of the modified grades, linked to a broader scattering range of as well tensile elongation as tensile strength. The decay in tensile properties at low moulding pressure is more critical for Standard PTFE than for the modified product version, a consequence of the better particle fusion of the modified PTFE. At very high pressure, powder flow in the crystalline regions leads to enhanced molecular orientation in flow direction. This effect makes the building up of a network formation through entanglements during sintering more difficult (Fig. 8-8).

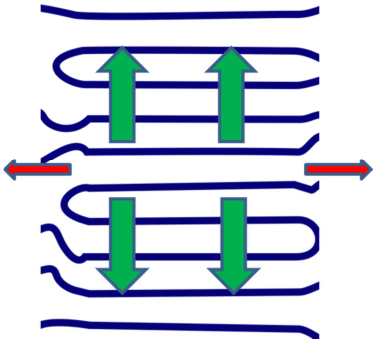


Figure 8-8: The formation of entanglements is hindered in polymers with parallel oriented molecular chains

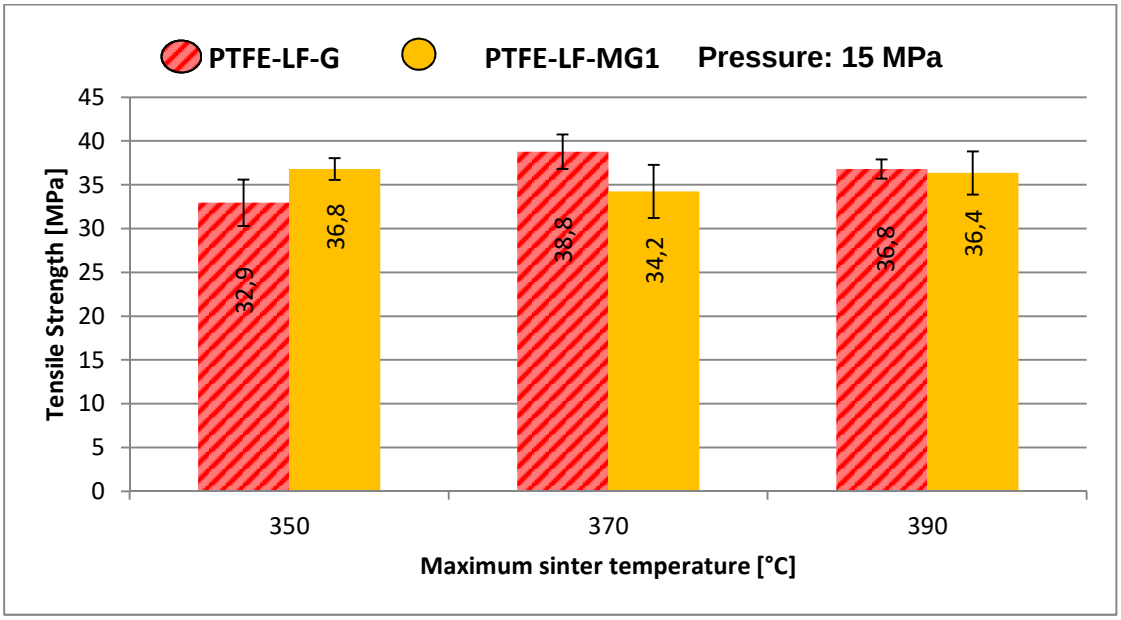


Figure 8-9: Impact of maximum sintering temperature on tensile strength for PTFE-LF-G and PTFE-LF-MG1

In this study the best results for PTFE-LF-G are at 370°C and for PTFE-LF-MG1 at 350°C. The standard sintering temperature is recommended to be 375°C. [9] For modified PTFE the values of 36.8 MPa and 36.4 MPa are an indication of improved particle fusion, whereas 34,2 MPa are below the typical values. For modified PTFE due to the reduced melt viscosity the best temperature is 370°C, while for Standard PTFE 375°C is the recommended temperature. At this slidely enhanced temperature the polymer gel achieves better flow characteristic, the fundament for good particle fusion.

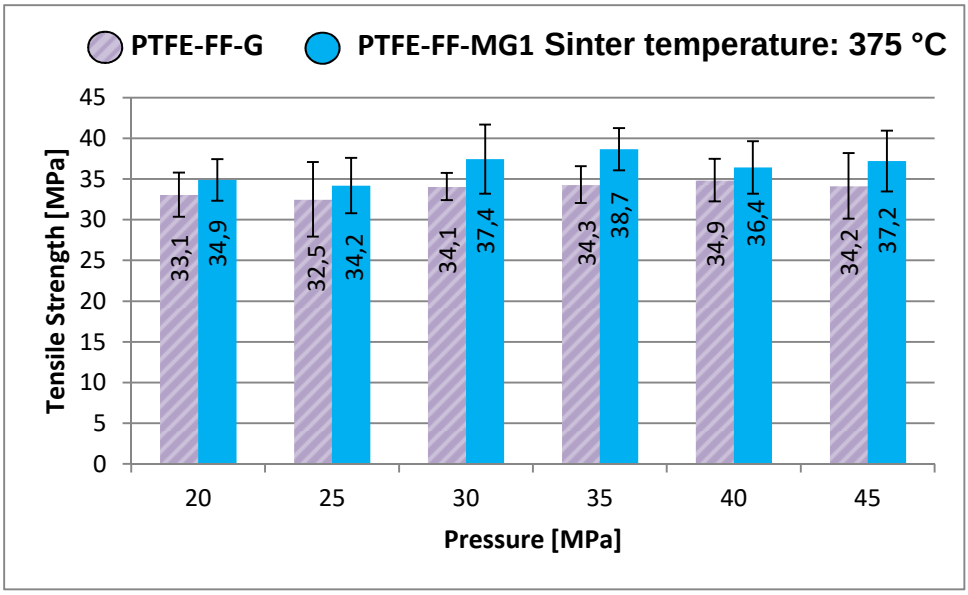


Figure 8-10: Impact of moulding pressure and tensile strength for PTFE-FF-G and PTFE-FF-MG1

For PTFE-FF-MG1 and for PTFE-FF-G the best results obtained are at around 35 (+/- 5) MPa with maximum values at moulding pressures of 30 respectively 40 MPa.The moulding pressure to 20 – 25 MPa yields in lower tensile strength values are reduced.

The origin for the different pressures required for low flow and for free flow materials can be seen from the particle pictures of these two different product lines, exemplified in figure 8-4 a and b. [7]

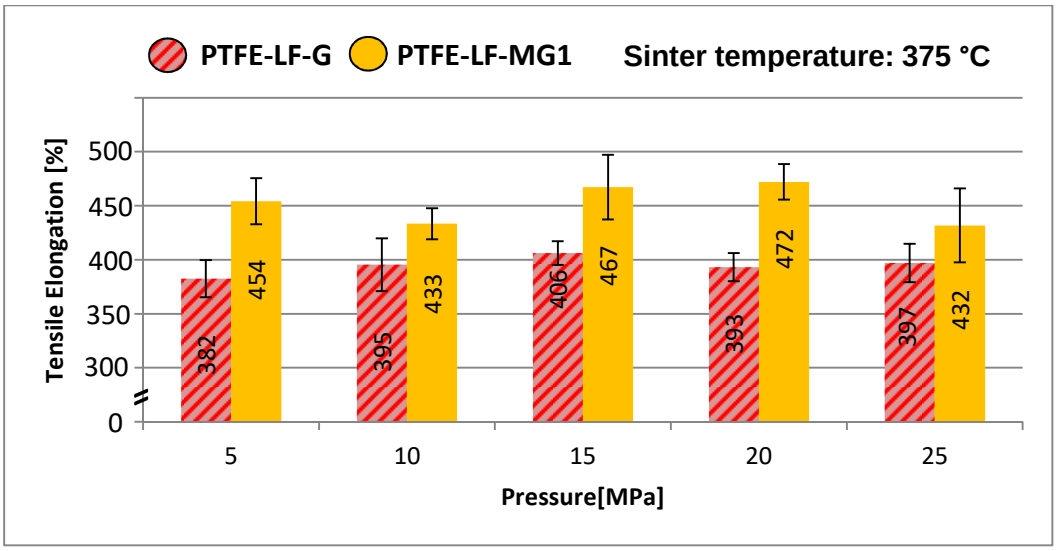


Figure 8-11: Impact of moulding pressure on tensile elongation at break for PTFE-LF-G and PTFE-LF-MG1

The tensile elongation as a function of moulding pressure is systematically higher for modified PTFE. Generally it can be stated, that the results are very similar although the moulding pressure has been varied in a very broad range. For production purposes this means,

that both materials are very tolerant against moulding pressure variations, when characterized by ultimate tensile elongation.

Different products generate different tensile stress-strain curves. In figure 8-12, the basic differences can be seen and the determination of yield strength, tensile strength and failure strength (ultimate strength) is shown. In this study the values for ultimate strength are taken.

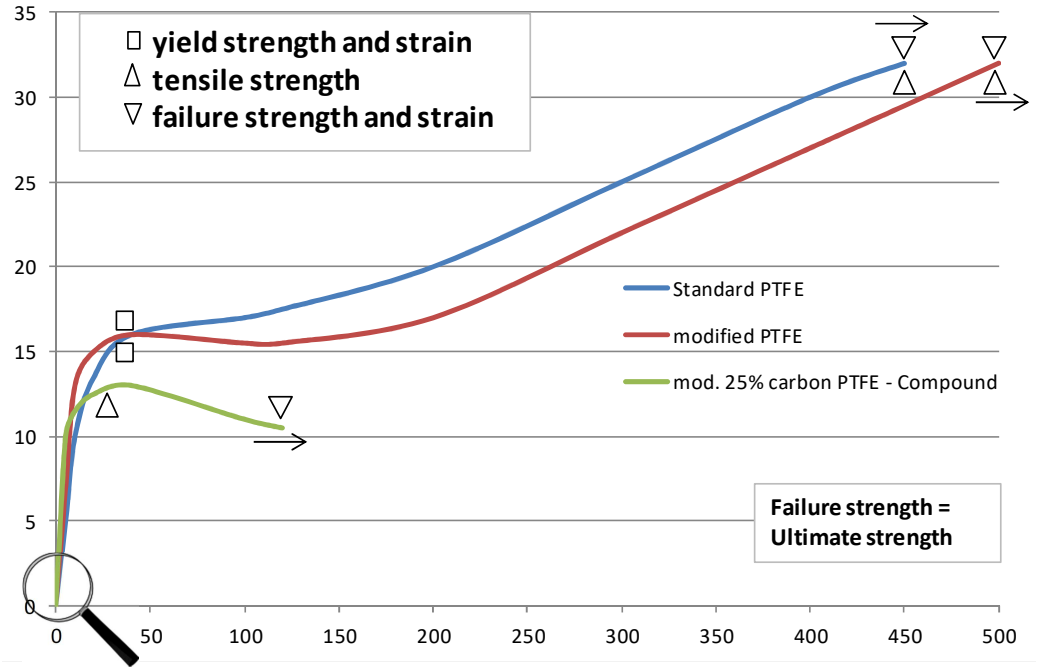


Figure 8-12: Stress-strain curves of Standard PTFE, modified PTFE and modified 25% carbon PTFE compound

As can be seen in figure 8-12 above the values for the different materials are very different, for Standard PTFE the tensile elongation is at about 500%, while for the modified PTFE compound the results are at 120%.

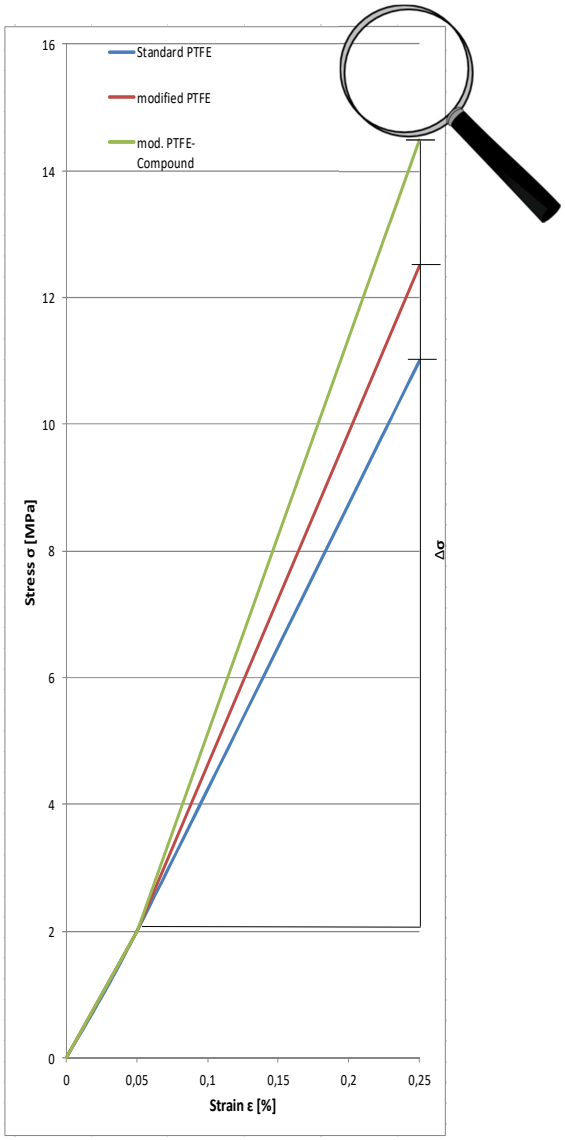


Figure 8-13: Enlargement of the strain-stress curve of Fig. 8-12 in the area of strain between 0.05 – 0.25 %

In figure 8-13 a detailled view on the area between 0.05 – 0.25% of strain is shown. In this area the modified PTFE compound has higher values for stress, while Standard PTFE material has the lowest. Thereby different values for the E-modulus are the result.

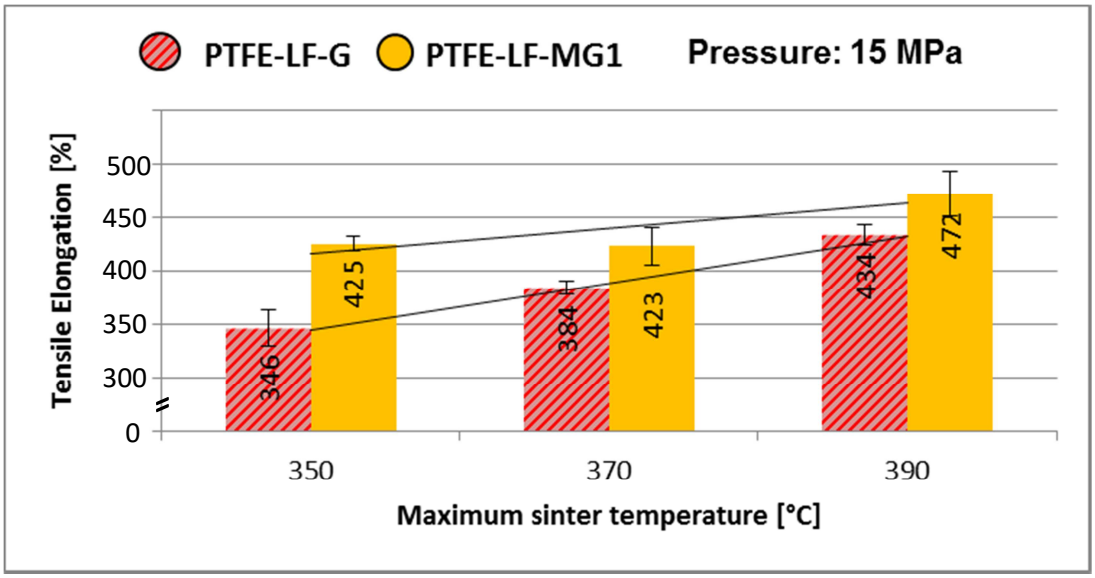


Figure 8-14: Impact of maximum sinter temperature on tensile elongation for PTFE-LF-G and PTFE-LF-MG1

Figure 8-14 shows, for modified PTFE tensile elongation is higher at all applied sinter temperatures. Both, modified and Standard materials, show the highest results at 390°C. For PTFE-LF-G results are increasing with sintering temperature. For PTFE-LF-MG1 the results are nearly the same at 350°C and 370°C and are further increasing when the sintering temperature goes further up. It can be said, that both materials are very tolerant to change of maximum sinter temperature. Obviously higher sinter temperature supports entanglement formation leading to a higher elongation at break as disentanglement becomes more difficult. Elongation at break is rather an important property for manufacturing processes than for applications. In exceptional cases higher elongation values make the assembly processes more safe. On the other side, increased elongation values can also be a first indication for over-sintering, due to easier disentanglement of the degraded, shorter molecular chains. The respect for the cold flow is important for applications with permament pressure load, like gaskets or the section for fixation of a dynamic moving membrane.

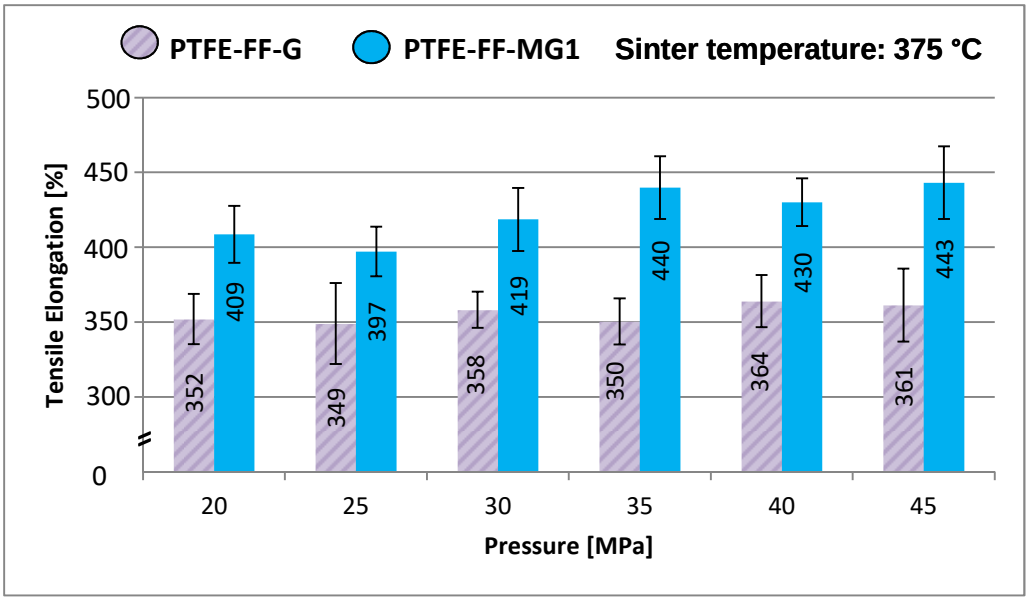


Figure 8-15: Impact of moulding pressure on tensile elongation for PTFE-FF-G and PTFE-FF-MG1

The tensile elongation is systematically higher for modified PTFE (Fig. 8-15). Both results are similar over the whole range of pressure adjustment. A tendency for higher elongation values for PTFE-FF-MG1 at enhanced pressure values can be observed but has no crucial role.

8.2.3 Investigation on density

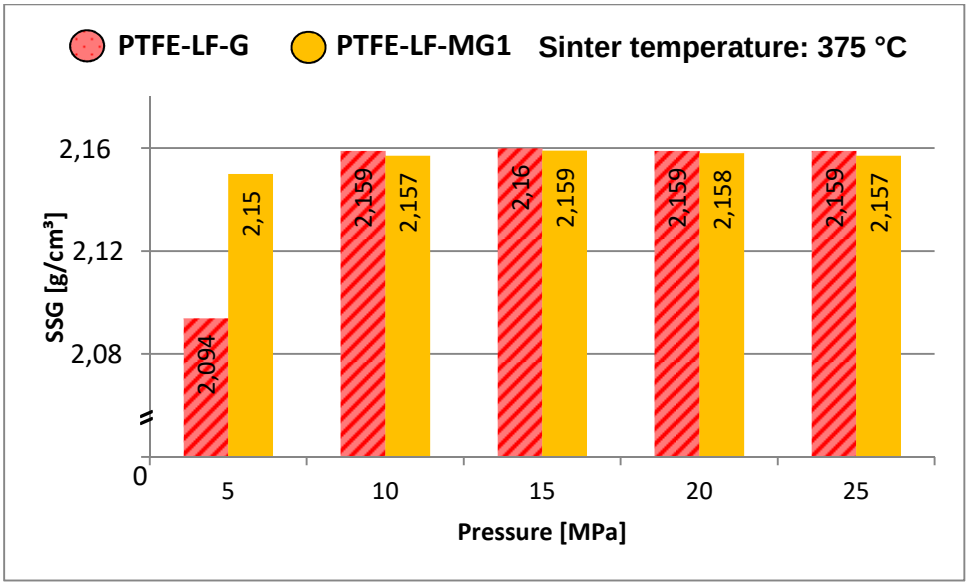


Figure 8-16: Impact of moulding pressure on SSG for PTFE-LF-G and PTFE-LF-MG1

The densities for PTFE-LF-G and PTFE-LF-MG1 have the best results at 15 MPa showing a high tolerance level for moulding pressure variations (Fig. 8-16): All results are close together for moulding pressure in the range of 10 MPa to 25 MPa. Moving even more to the low

pressure side by applying 5 MPa only, Standard PTFE shows a significant decay in SSG while modified PTFE still remains on a high level. Origin is the better particle fusion of modified PTFE, even under low pressure. The decay of the density of PTFE-LF-MG1 at 5 MPa is caused by void formation due to un-sufficient particle fusion. The effect can be seen in the figure 8-17a drastically.

During the processing of Standard and modified PTFE it could be observed in rare cases, that with the increase of moulding pressure SSG decreases. This phenomenom goes back to air entrapment due to hindered outgassing. It did not become visible in these tests as obviously there is no air entrapment happening under the applied careful moulding conditions which left enough time for outgassing. Additionally the relatively small size of the test billets used supports outgassing further.

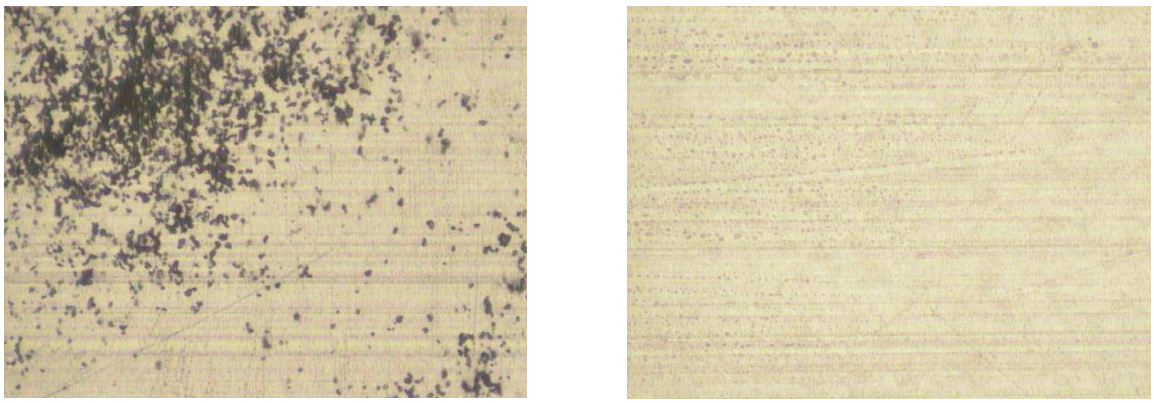


Figure 8-17: PTFE-LF-MG1 with moulding pressure at a) 5 MPa and b) 25 MPa

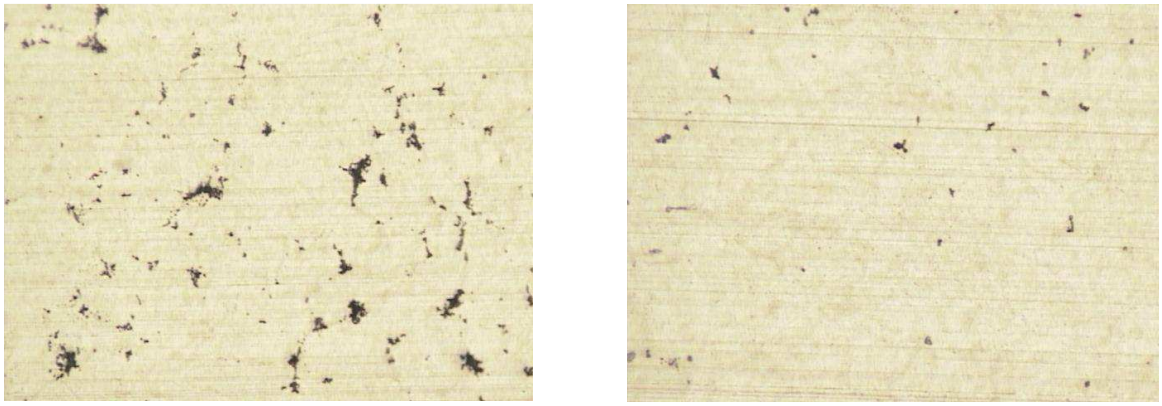


Figure 8-18: PTFE-FF-MG1 with moulding pressure at a) 20 MPa and b) 35 MPa

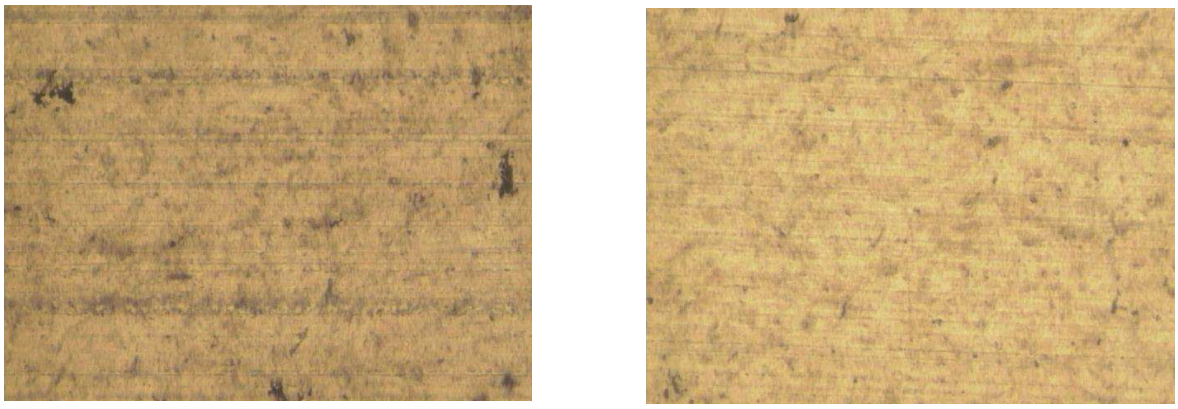


Figure 8-19: PTFE-FF-G with moulding pressure at a) 20 MPa and b) 35 MPa

Pictures in fig. 8-17 – 8-19, made from thin skived film of the individually processed polymers, demonstrate the variations in particle fusion depending on the moulding pressure: If the moulding pressure is set too low for the polymer of concern, the particles do not show a compact polymer structure in the visual inspection. Numerous voids are entrapped inside the polymer material. This is true for both materials PTFE-LF-MG1, as well as PTFE-FF-MG1. Whenever the moulding pressure is set too low, quality of the polymer obtained must be considered to be worse.

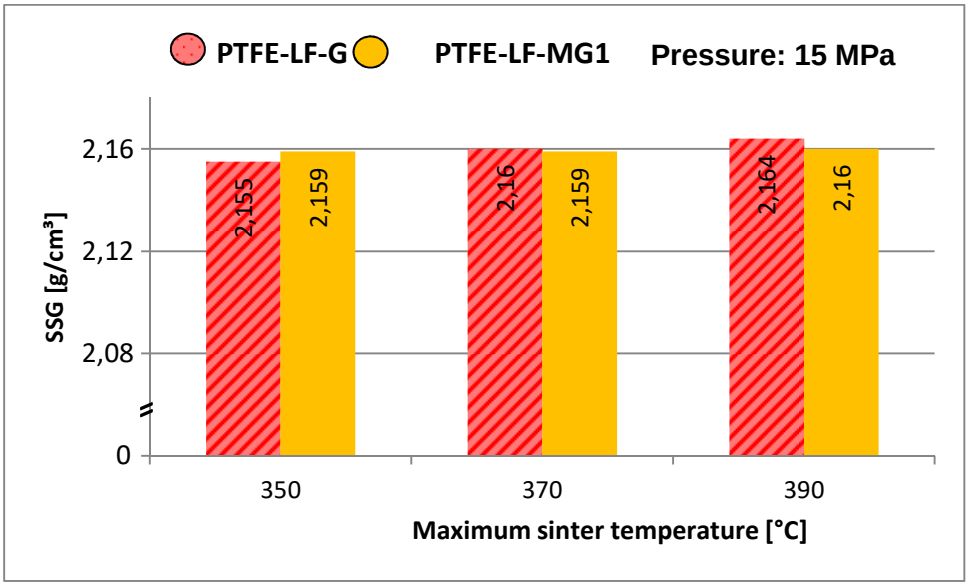


Figure 8-20: Impact of maximum sinter temperature on SSG of PTFE-LF-G and PTFE-LF-MG1

Figure 8-20 shows, that the maximum sinter temperature of 350°C is too low for PTFE-LF-G, but not for PTFE-LF-MG1, due to improved particle fusion. The PPVE content for this type of modified material is at about 0.1 wt%. [48] PTFE-LF-G of this density will definitely show voids inside. At 370°C the values are as expected. At 390°C the increased density of PTFE-LF-G at this temperature can be explained as follows: Particle fusion at 370°C was not completed. Further increase of the maximum sintering temperature by 20 °C up to 390 °C yields in excellent particle fusion, thus enhancing SSG from 2.155 at 350°C to 2.164 g/cm³ at 390°C (Fig. 8-20).

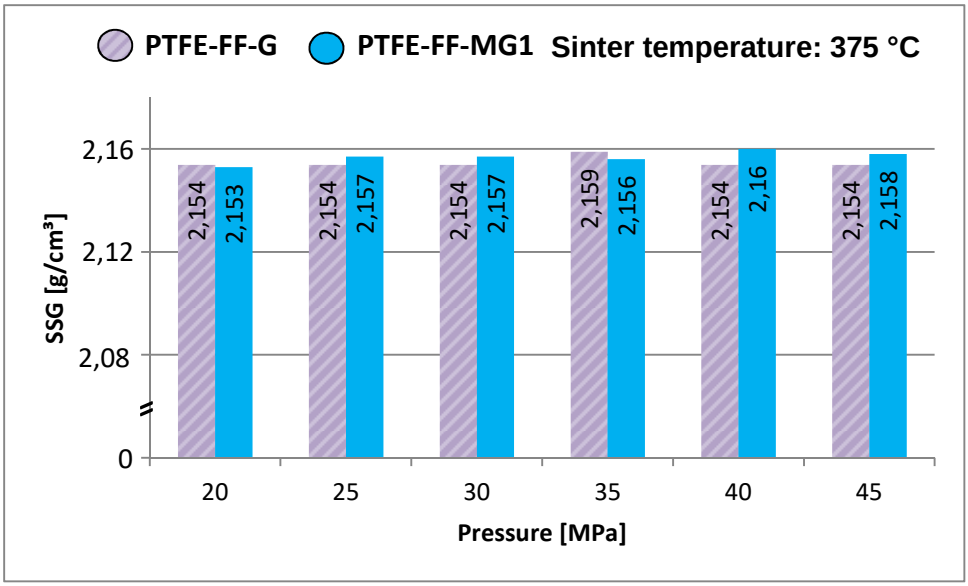


Figure 8-21: The impact of moulding pressure on SSG for PTFE-FF-G and PTFE-FF-MG1

For PTFE-FF-G the best result can be found at 35 MPa, whereas other results, obtained from lower moulding pressure as well as from a higher one, show slightly decreased SSG-values. For PTFE-FF-MG1 best result is at 40 MPa, other results (except that one obtained from 20 MPa moulding pressure) show a trend to be slightly enhanced compared to the values of the Standard goods. Both materials are extremely tolerant against moulding pressure variations. In case of very low moulding pressures in the range of 20 MPa the beginning of SSG-decay can be observed.

The findings are the result of the compensation of reduced particle compaction by low-pressure moulding through the dominating Laplace pressure arising during sintering: in case voids are remaining between the particles after moulding at low pressure, these are closed by particle fusion during sintering, driven by Laplace pressure. In the contact areas between the powder particles, generated by the moulding process, inter-diffusion of molecular chains of different particles will establish the bonding force between the particles during sintering. The contraction force between the particles, driven by the target to achieve a minimum of void surface, the so-called Laplace-pressure, will ensure good particle adhesion and void-closure, even if the compaction due to low moulding pressure was less sufficient. [18]

As a benefit for the processor, PTFE processing is not critical for local pressure variations inside the mould. But lower moulding pressure generates higher shrinkage during sintering. This effect can be considered to be the main origin for internal stress generated inside PTFE billets when moulded under different pressure at different locations. After sintering the material is very homogenious with regard to SSG. Significant levels of internal stresses can cause product warpage or even crack formation and consequently should be released by post annealing temperature treatment of the part. For semi-crystalline polymers temperature for stress relieve by post annealing is recommended to be between T_G and T_M, closer to the T_M side (for Standard and modified 250 - 290°C).

8.2.4 Shrinkage measurements

The shrinkage is an important value for the defined dimensions of the part and the correlation between the design and the finished size. The absence of pores is a major factor as well as the calculable shrinkage in connection with the tolerances.

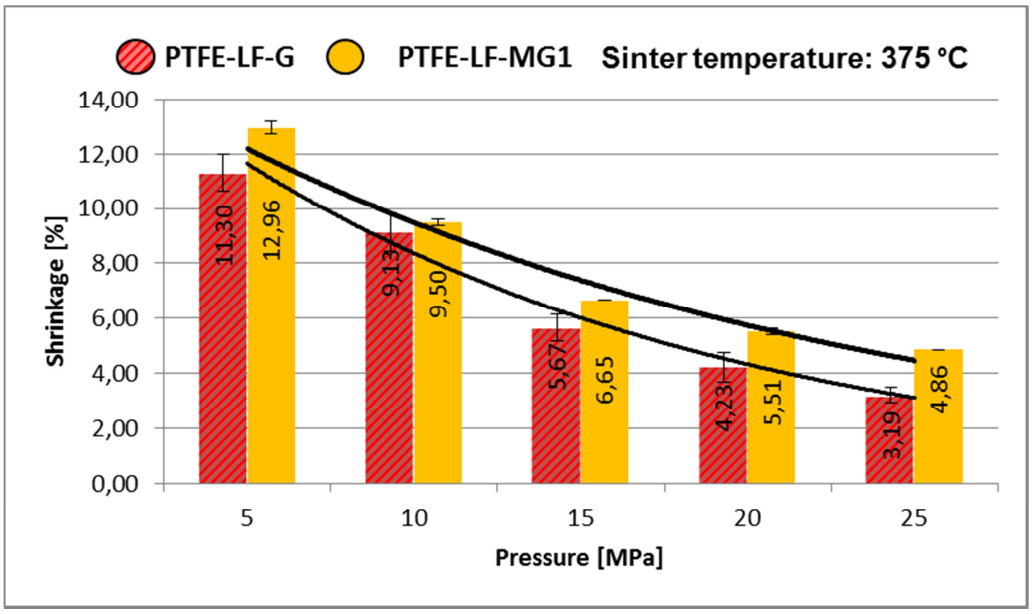


Figure 8-22: Impact of moulding pressure on shrinkage for PTFE-LF-G and PTFE-LF-MG1

The shrinkage is systematically decreasing with higher pressure and there is less shrinkage for PTFE-LF-G than for PTFE-LF-MG1 (Fig. 8-22). The higher the moulding pressure, the lower the free volume between the particles. As a consequence the shrinkage is decreasing with increasing moulding pressure. Taking very well into consideration that the degree of porosity after moulding is slightly enchanced for PTFE-LF-G (0.75%) over PTFE-LF-MG1 (0.4%), and the particle size is the same for both materials, PTFE-LF-MG1 show a higher shrinkage compared to PTFE-LF-G because of following two reasons:

- Different polymer morphology
- Higher energy absorption during powder milling in case of modified PTFE gives the non-sintered polymer a higher degree of orientation, which is the cause for the enhanced shrinkage during sintering as a consequence of the entropy-driven recovery mechanism. The shrinkage increases with rising maximum temperature. The higher the temperature, the better the particle fusion and elimination of free volume to a higher degree.

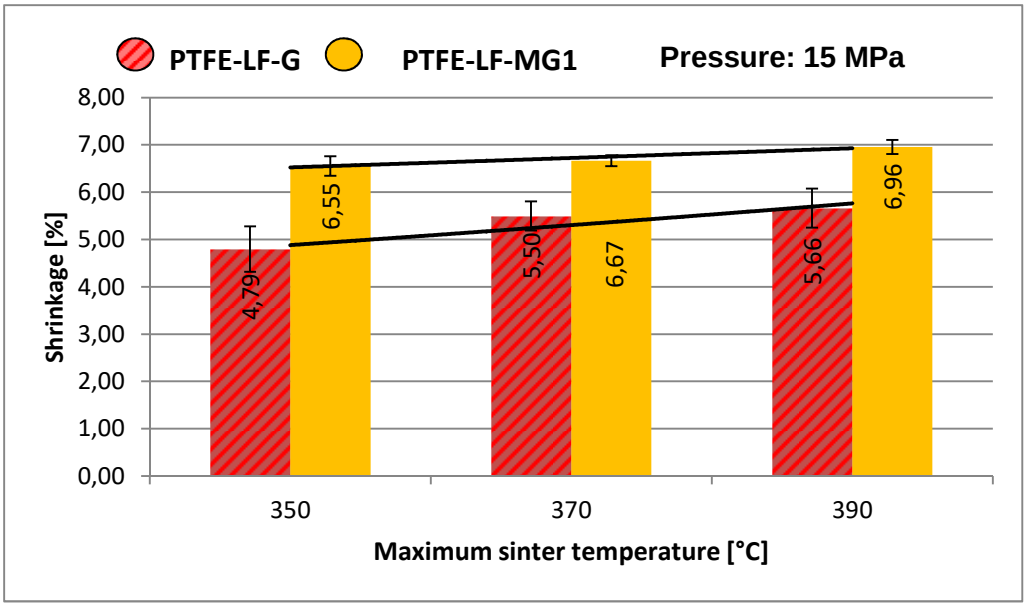


Figure 8-23: Impact of maximum sinter temperature on shrinkage for PTFE-LF-G and PTFE-LF-MG1

The results at different temperatures are close together (Fig. 8-23). The highest values are at 390°C, maybe considered as an indication for best polymer compaction. If, as a theory, 390°C is considered to be the temperature of beginning polymer decomposition, the resulting reduced molecular weight has a tendency for higher degree of crystallization which also contributes to higher shrinkage. The shrinkage decreases with higher moulding pressure because the particle compaction is improved. As a consequence the particle fusion is also better. For modified PTFE the shrinkage is higher because for milling the PTFE particles more energy is necessary. Consequently the milled particles of modified PTFE are characterized by higher degree of molecular orientation. During sintering, the orientation of the molecules is reduced and is targeting the isotropic distribution of randomly wounded structure.

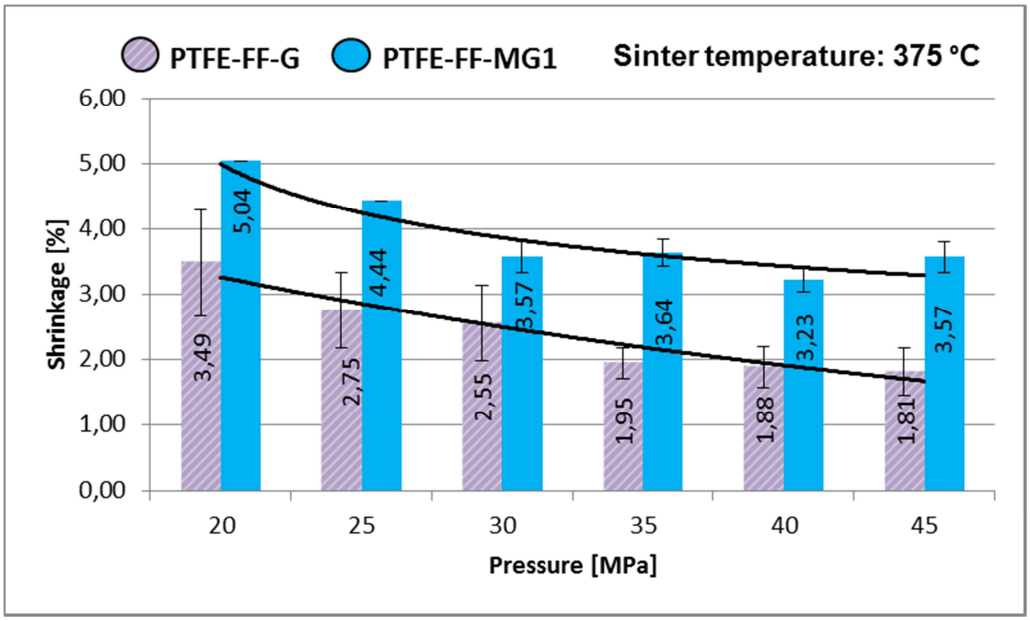


Figure 8-24: Impact of moulding pressure on shrinkage for PTFE-FF-G and PTFE-FF-MG1

The shrinkage systematically decreases with higher pressure - less shrinkage for PTFE-FF-G than for PTFE-FF-MG1. The slope of shrinkage decay with higher pressure is decreasing (Fig. 8-24).

8.2.5 Differential Scanning Calorimetry Analysis

					1. Fuison			Cooling			2. Fusion		
material	pressure (Kg/cm²)	sintering temperature (°C)	Cooling speed [°C/min]	weight [mg]	Peak [°C]	Area [J/g]	Δ H [J/g]	Peak [°C]	Area [J/g]	Δ H [J/g]	Peak [°C]	Area [J/g]	Δ H [J/g]
PTFE-LF-G	150	350	10	12,756	330,44	23,82	23,8199	311,41	-23,522	-23,5225	329,18	23,979	23,9792
	150	370	10	14,501	330,67	39,507	29,5071	310,95	-24,728	-24,728	329,31	23,316	23,3161
	150	390	10	12,788	330,55	30,794	30,7935	310,11	-26,975	-26,9749	329,35	26,127	26,1274
		DSC											
	150	410	10	13,292	330,55	35,52	26,7225	310,46	-25,1402	-33,42	329,15	32,16	24,19
	150	430	10	13,91	330,24	37,1	26,67	310,13	-34,42	-24,74	329,13	34,04	24,47
PTFE-LG-MG1	150	350	10	14,02	327,1	28,547	28,5471	304,93	-26,158	-26,1576	324,65	27,222	27,2223
	150	370	10	13,385	327,03	30,704	30,7041	304,13	-26,067	-26,0667	324,97	27,981	27,9807
	150	390	10	14,087	327,61	31,329	31,3288	303,47	-25,3	-25,2997	325,13	26,659	26,6592
		DSC											
	150	410	10	14,709	327,52	50,77	34,51	303,83	-46,55	-31,65	324,76	46,28	31,46
	150	430	10	14,724	327,35	42,81	29,08	303,65	-43,26	-29,38	324,93	42,37	28,77

material	pressure (Kg/cm²)	sintering temperature (°C)	Cooling speed [°C/min]	weight [mg]	Peak [°C]	Area [J/g]	Δ H [J/g]	Peak [°C]	Area [J/g]	Δ H [J/g]	Peak [°C]	Area [J/g]	Δ H [J/g]
PTFE-LF-G	150	375	1	14,908	330,71	40,19	26,96	315,65	-40,84	-27,39	330,43	42,4	28,44
	150	375	5	14,413	330,76	38,78	26,9	312,8	-33,24	-23,07	329,62	34,81	24,15
PTFE-LF-MG1	150	375	1	13,805	327,45	42	30,42	309,33	-42,58	-30,85	326,62	42,89	31,07
	150	375	5	14,449	327,45	43,71	30,25	305,97	-36,43	-25,21	325,28	38,12	26,38

Table 8-3: Overview of DSC-analysis

Running the sintering temperatures of 410°C and 430°C as an upper limit can not be performed as standard process in a sintering oven because of safety reasons. Therefore the measurements under constructive conditions were performed by using DSC technique. The results can be seen in table 8-3. [61]

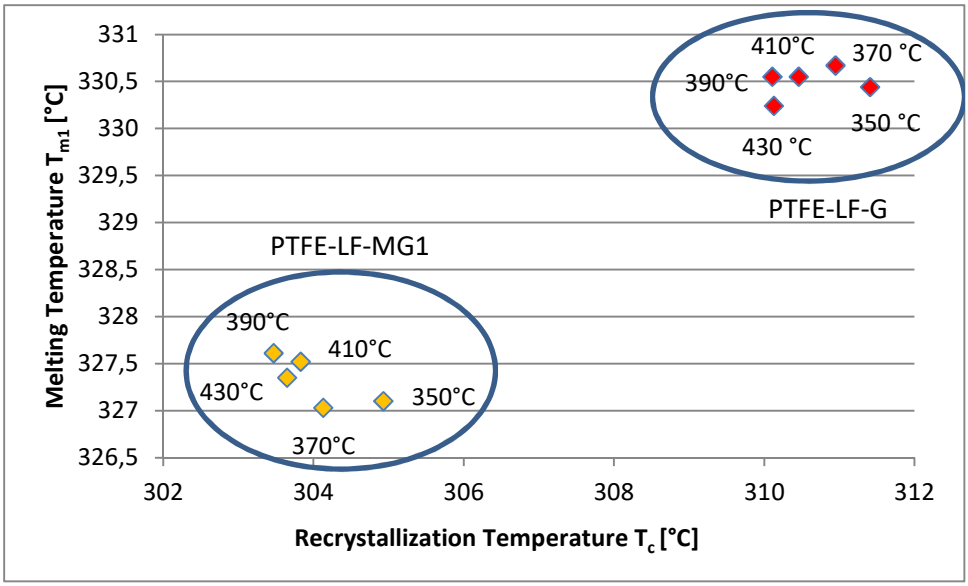


Figure 8-25: Recrystallization temperature and melting temperature for PTFE-LF-G and PTFE-LF-MG1 determined by DSC

Figure 8-25 above shows the correlation between the temperature of recrystallization and the melting temperature in reference to the maximum sinter temperature. For PTFE-LF-MG1 the values for the melting temperature as well as the temperature of recrystallization are lower than for PTFE-LF-G. The consequence for the industrial processing of both products is, that different temperature programs for sintering are needed: during cooling a temperature dwell step should be set at temperatures just beneath the recrystallization temperature of the individual product.

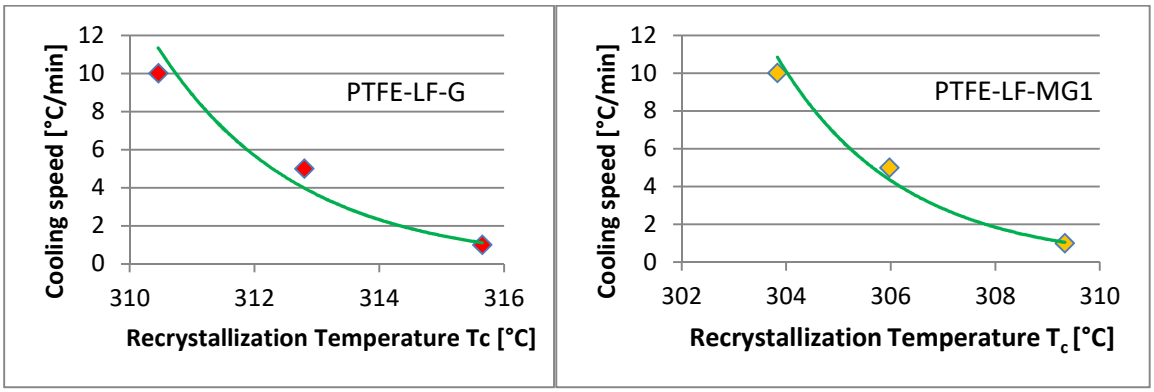


Figure 8-26: Temperature of recrystallization as a function of cooling speed for a) PTFE-LF-G and b) PTFE-LF-MG1

For the recrystallization temperature and the cooling speed figure 8-26 a and b, both have a decreasing curve progression, the lower the cooling speed, the higher the recrystallization temperature. There are two reasons for this effect. The recrystallization temperature of the modified PTFE is lower, because the side chain of the PPVE monomer disturbes the crystallization and thus delays the beginning of the recrystallization. The second reason is due to the cooling speed. As typical for high molecular weight polymers and its difficulty for

forming crystallites, the material has to be transformed from the gel phase into the state of "supercooled melt" that the seed formation of the recrystallization process can begin.

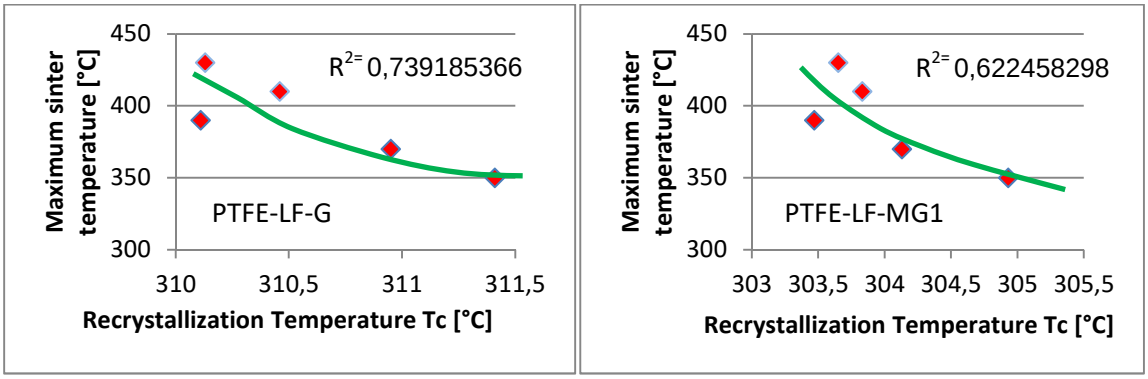


Figure 8-27: Recrystallization temperature and maximum sinter temperature for a) PTFE-LF-G and b) PTFE-LF-MG1

As already determined for the cooling speed, also the recrystallization temperature is increasing with decreasing maximum sinter temperature (Fig. 8-27 a and b).

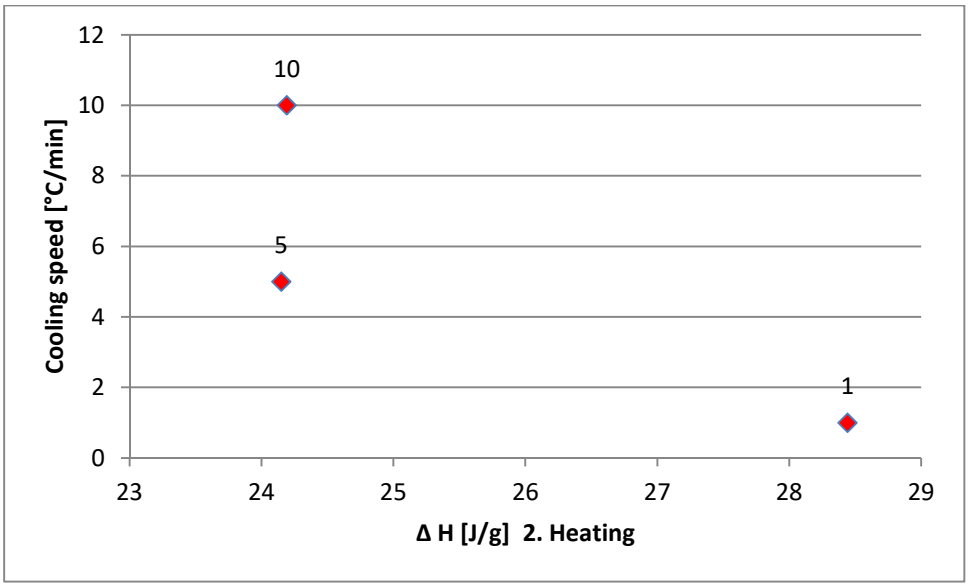


Figure 8-28: Δ H [J/g] of 2nd heating and cooling speed for PTFE-LF-G

The cooling speed of 1°C/min, 5°C/min and 10°C/min was measured in order to analyze the impact of recrystallization on material characteristics (Fig. 8-28). DSC was also done with 410°C and 430°C, but holding time only for 1 min, which is definitely too short to find the real influences. Normally 430°C is considered to be a critical temperature for the PTFE, but these results indicate that a one minute short-term exposure to 430°C will not have a measurable negative impact. This enhances the safety aspects in processing with PTFE. During inline sintering processes as used for manufacturing of PTFE tubes or PTFE wire insulations short term sinter temperatures up to 450°C with object temperature of 430°C are state of the art.

material	pressure (Kg/cm²)	sintering temperature (°C)	cooling speed [°C/min]	cooling peak [°C]
PTFE-LF-G	150	375	1	315,65
	150	375	5	312,8
	150	375	10	310,46
PTFE-LF-MG1	150	375	1	309,33
	150	375	5	305,97
	150	375	10	303,83

Table 8-4: Overview of PTFE-LF-G and PTFE-LF-MG1 with different cooling speed

8.3 Setting up a guideline for material selection

As a result of all measurements and characterization a guideline for a material selection and process optimization as a suggestion for different applications can be made. The guideline shows all materials with the different moulding pressures and maximum sinter temperatures as well as the evaluation results of tensile strength, tensile elongation, SSG and shrinkage. For each measurement result a trend is pointed out in terms of reduced, average and improved.

So depending on which application and in this context needed values, the optimized processing technology for the finished product can be choosen.

		Evaluations						
Material	Pressure (MPa)	Maximum sinter temperature (°C)	Bulk density [g/L]	Tensile Strength [MPa]	Tensile Elongation [%]	SSG [g/cm³]	Shrinkage [%]	
PTFE-LF-G	5	375	370 - 400	↓	→	↓	↓	↓ Reduced
	10	375	370 - 400	↓	→	→	↓	→ Average
	15	375	370 - 400	↑	↑	↑	→	↑ Improved
	20	375	370 - 400	→	→	→	↑	
	25	375	370 - 400	→	→	→	↑	
	15	350	370 - 400	→	↓	↓	↑	
	15	370	370 - 400	↑	→	→	→	
	15	390	370 - 400	→	↑	↑	↓	
PTFE-LF-MG1	5	375	370 - 400	↓	→	↓	↓	
	10	375	370 - 400	↓	→	→	↓	
	15	375	370 - 400	↑	↑	↑	→	
	20	375	370 - 400	→	↑	→	↑	
	25	375	370 - 400	→	→	→	↑	
	15	350	370 - 400	↑	→	→	↑	
	15	370	370 - 400	→	→	→	→	
	15	390	370 - 400	→	↑	↑	↓	
PTFE-FF-MG1	20	375	800 - 900	↓	→	↓	↓	
	25	375	800 - 900	↓	→	→	↓	
	30	375	800 - 900	↑	→	→	→	
	35	375	800 - 900	↑	→	→	→	
	40	375	800 - 900	→	↑	↑	↑	
	45	375	800 - 900	→	→	→	↑	
PTFE-FF-G	20	375	800 - 900	↓	→	→	↓	
	25	375	800 - 900	↓	→	→	↓	
	30	375	800 - 900	→	→	→	→	
	35	375	800 - 900	↑	↑	↑	→	
	40	375	800 - 900	↑	→	→	↑	
	45	375	800 - 900	→	→	→	→	

Table 8-5: Guideline for material selection and process optimization

The guideline (Tab. 8-5) above can give detailed informations for the material selection and the process optimization, depending on the targeted application. Some examples are:

- Liners in chemical industry because of their stability against corrosion and temperature – physical properties are less important than the chemical structure of the material, for example better particle fusion. Also a higher sinter temperature can be recommended because of the better compaction and particle fusion, higher SSG, which causes higher crystallinity and so better barrier effect. (Recommended material: PTFE-LF-MG1 moulded at 15 MPa)
- Bellows and membranes are another application where PTFE and modified PTFE are used because of its good flex life. Additionally a low permeability by the use of modified PTFE is recommended. There must be a certain pressure resistance in loading area, so good mechanical properties like tensile strength is recommended for low creep. Also the physical properties for this dynamic application are important because the part unterlies a constant load. (Recommended material: PTFE-LF-MG1 moulded at 15 MPa, low SSG batch preferred, with rapid cooling [9])
- The free flow material Standard and modified is the preferred material for producing semi-finished parts like sheets. The powder is used more economic in processing and can be calculated more efficient than the low flow material. (Recommended material: PTFE-FF-G moulded at 35 MPa)

The internal stresses in the material after sintering are subject to post heat treatment, whenever it is required to manufacture parts with high dimensional accuracy. In such cases pre-machining is performed followed by heat treatment before the final machining step is carried out. Post crystallization is not observed in PTFE, neither for Standard nor for modified.

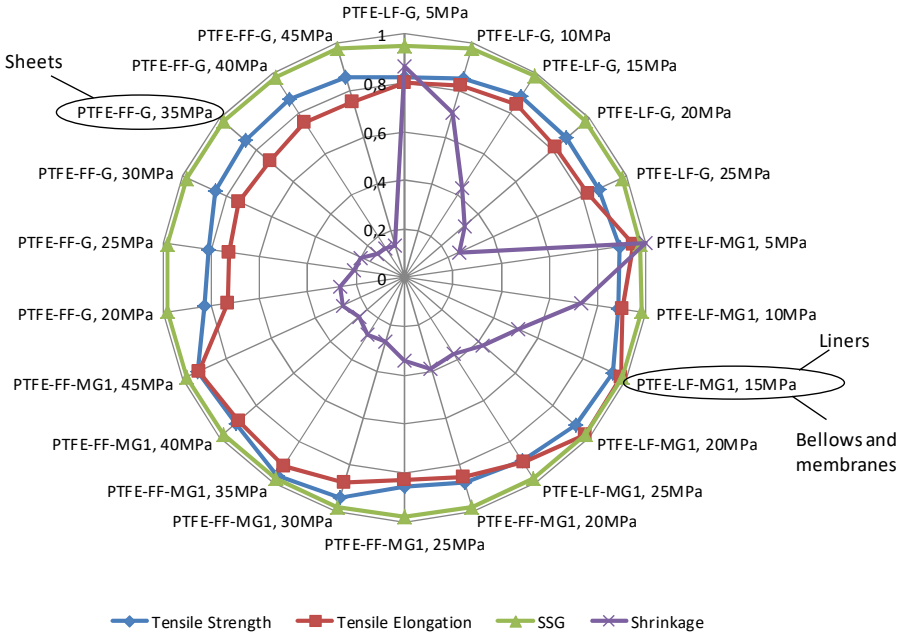


Figure 8-29: Web-guideline for PTFE-FF and LF-materials at different pressures

Additionally to table 8-5 the guideline for material selection figure 8-29 and 8-30 show network diagrams to give a clear view and comparison between the different materials in their

mechanical properties depending on different pressures and temperatures. Outstanding in the figure above are the low flow materials at a pressure of 5 MPa and the outstanding shrinkage. This shows, that the pressure of 5 MPa is not adequate for a homogenious and processable structure, as already mentioned in this chapter before. Also the free flow materials have in general a lower shrinkage than the low flow PTFE materials. The density for all materials is comparable. As 5 MPa moulding pressure is not sufficient for the perfect powder compaction the physical properties are worse. The best results for tensile elongation and tensile strength can be seen at the modified FF and LF materials.

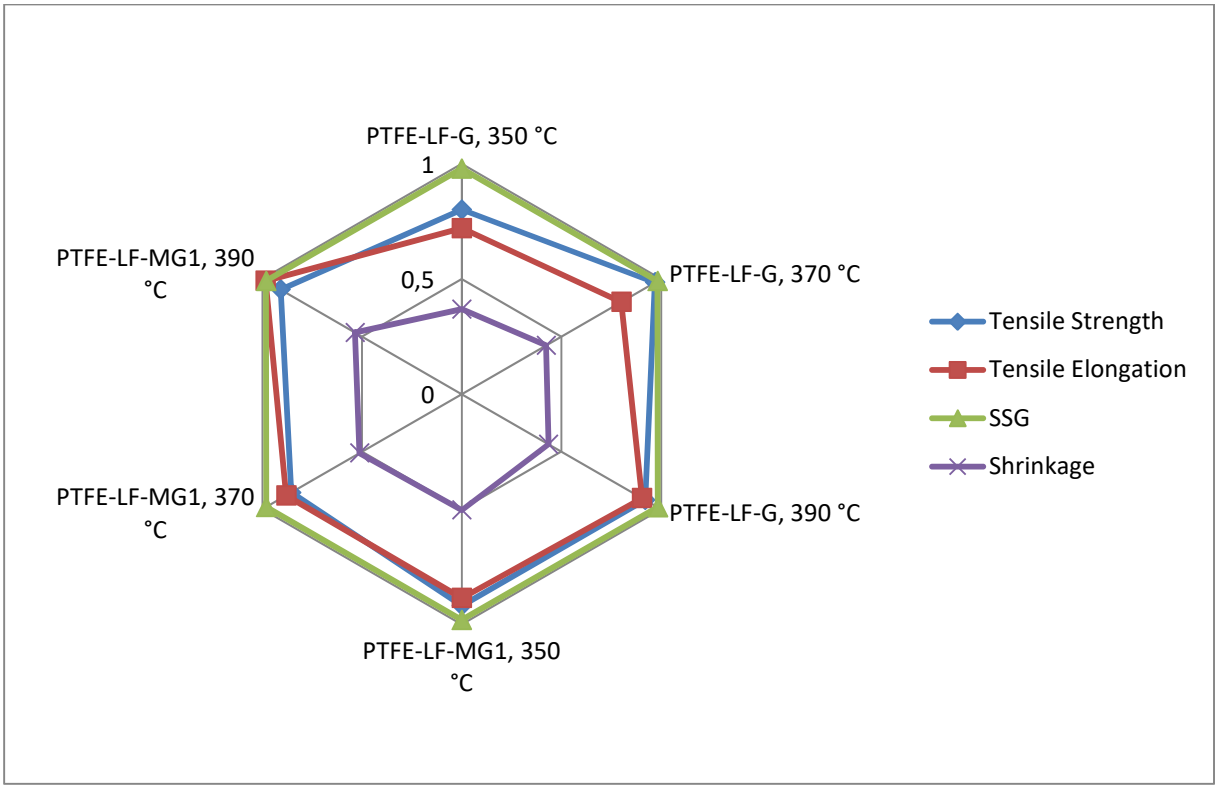


Figure 8-30: Web-guideline for PTFE-LF at different temperatures

The different temperatures for low flow Standard and modified materials are also shown in a cleary arranged way, although the differences are not that high.

In this chapter four materials, free flow and low flow, modified and Standard, were analyzed regarding chemical and physical properties to create a guideline for material selection and process optimization. Based on the impact of processing technology and the material characterization suggestions for further applications will be made.

9 PTFE compounds –Systematic approach on the impact of selected fillers and filler combinations

The most significant commodities are filled compounds of PTFE because of the large volume of consumption. There are some manufacturer who produce their own compounds inhouse while others purchase from speciality compounders. These compounders are skilled in formulation and production of various filled compounds. Standard pure and unfilled PTFE is inadequate for a number of mechanically demanding engineering applications, but the so called cold flow would prevent the use of PTFE in many mechanical applications. For the first time in the 1960s the addition of fillers was found to improve a number of physical properties of PTFE, particularly creep and wear rate. For applications in gaskets, shaft seals, bearings, bearing pads and piston rings filled PTFE is very suitable. Further advantages are chemical resistance, low friction, high temperature resistance combined with mechanical requirements. [18]

	Filler						
Property	**Glass fiber (up to 40%)**	**Carbon (up to 35%)**	**Carbon coke (up to 35%)**	**Graphite (up to 15%)**	**MoS_2 (up to 5%)**	**Bronze (up to 60%)**	**Steel (up to 60%)**
Wear	↘	↘	↘↘	↘	→	↘↘	↘
Abrasion	↘	→	→	↘	↘	→	↘↘
Chemical stability	↘	↘	↘	↘	↘	↘	→
Thermal conductivity	→	↗	↗	↗	→	↗	↗
Sliding property	→	→	→	↗	↗↗	→	→
Coefficient of friction	↘	↘	↘	↘	↘	↘	↘
Hardness	↗	↗	↗↗	↘	→	↗	↗
Stiffness	↗	↗	↗	→	→	→	→
Dry running conditions	→	↗	↗	↗	↗	→	→
	Trends:	blue =	neutral	green =	positiv	red =	negative

Table 9-1: Effect of fillers on material properties [9]

Table 9-1 above show the effects of the different fillers clearly and the corresponding trends, in a positiv, negative or neutral way. The direction of the arrows show if the filler increases, decreases or does not change the property of the material.

The filler carbon reduces the creep, increases hardness, elevates thermal conductivity of PTFE and has some electrical conductivity. If the carbon is combined with graphite particularly the wear resistance is improved. This combined compounds performs well in non-lubricated applications such as piston rings in compressor cylinders. To achieve close tolerances during machining the wear rate of the tool must be reduced by using a softer carbon powder. Carbon fibers lower the creep and increase flex and compressive modulus, as well as hardness. To achieve this changes glass can be combined but reduced amount carbon fiber can have the same effects. Carbon fiber is inactive to both hydrofluoric acid and strong bases which react with glass. For compounds of carbon fiber the coefficient of thermal expansion is lowered and thermal conductivity is higher. Parts out of carbon fiber are lubricated with water, that is,

wear rate decreases, making them fitting perfectly for automotive applications in shock absorbers and water pumps. [26]

Due to the low friction characteristics of graphite, graphite filled PTFE has an extremely low coefficient of friction and is chemically inert. Furthermore it incorporated in combination with other additives such as carbon and glass and has excellent wear properties, especially against soft metals and high PV-values to PTFE.

The most popular metallic filler is bronze, although steel powder is occasionally used and it reduces deformations under load and raise thermal and electrical conductivity. These two characteristics can be especially important to applications where a part is subjected to load at extreme temperatures like air-conditioner compressor seals and transmission. Bronze is an alloy of chopper and tin and attacked by acids and bases. It also oxidizes and discoloures during the sinter process with no impact on the quality. But also nonoxidizing grades are available from some suppliers. [18]

Another additive is Molybdenum disulfide (MoS_2), which increases the hardness of the surface while decreasing friction. In opposite to that electrical properties are virtually unaffected. Normally it is used in small proportions and in combination with other fillers such as glass. This filler also reacts with oxidizing acids and is inert towards most other chemicals.

For other applications there can be used other fillers incorporated in PTFE like calcium fluoride which can replace glass in end-uses where glass is attacked by chemicals, or alumina which is an excellent electrical insulator and improves the mechanical properties of the compound for use in high voltage components. To impart colour to PTFE compounds for customization or ease of identification of parts, inorganic pigments can be added, which are able to withstand sintering temperatures. [26]

The aim for the production technique is to produce a uniform blend of PTFE with fillers that can be processed in the same moulding equipment.

Compound type	Unfilled PTFE	15% Glass Fiber	60% Bronze	23% Carbon/ 2% Graphite
Thermal conductivity [W/(m*K)]	0,24	0,33	0,57	0,58

Figure 9-1: Thermal conductivity of compounds [18]

As a representative example for thermal conductivity is the filler carbon/graphite with a high value for a conventional compounds (Fig. 9-1). In comparison to unfilled PTFE the deformation under load decreases for all filled compounds. As already mentioned above the combination of carbon and graphite reduce deformation at room temperature and elevated temperatures. At second position in this ranking 60% bronze by weight is the next effective filler in reducing deformation under load. Bronze, carbon and graphite increase the hardness. The effects on chemical properties depends on the type of the filler and the specific chemicals, but in general, they are such as good as those of the unfilled PTFE. [18]

For the tribological properties it can be said, that wear and friction are two independent and mutually exclusive variables. Unfilled PTFE normally has an extremely low coefficient of friction and a high wear rate. Fillers and filler combinations do not effect the coefficient of friction while the wear rate of the compound is reduced. The surface of the counter part may have a high wear rate as a result of abrasion, while that of the PTFE compound is small. As a function of type, concentrations and morphology of the fillers abrasion is strong. In the following chapters the wear rate and the coefficient of friction will be considered closely. Many variables like load, velocity, type of movement, degree of coverage, temperature, filler, finishing parts, break-in conditions, material surface, lubrication, environment and the presence of wear debris define a function for wear, friction and abrasion in general. The coefficient of friction is inversely proportional to pressure and proportional to velocity. Wear of compounds of PTFE is proportional to load (P) and velocity (V). [26] Combinations of pressure and velocity are defined where the material can be used, thus a PV limit is defined. Above this PV limit, the wear increases exponentially because of the heat generated as a result of motion. An example for calculated PV-values of a racing bike application is in the range of 0.16 – 0.29 (N/mm^2 * m/s), this means for P_{sit}: 0.9 N/mm^2, V_{sit}: 0.18 m/s and P_{stand}: 6.0 N/mm^2, V_{stand}: 0.05 m/s.

The wear behaviour of compounds is impacted by the characteristics of the filler and its content. Particle size, shape and structure are the key contributing filler variables. Coefficient of the friction of the compound is only sligthly effected by the filler, while wear factor is a strong function of the filler. It is difficult to make general conclusions from the performance of one filler under one set of conditions to others. For example, under moderate wear conditions, bronze does not perform as well as glass fiber. [18]

As a definition PTFE compounds are Standard or modified PTFE with fillers or different enhancements. PTFE compounds are like unfilled S-PTFE available as free flowing and low flowing powders. As already mentioned some inherent weaknesses of PTFE may be reduced by the use of modified PTFE.

In the following there are some examples for PTFE compounds [18]:

- **glass fibers**
    - Higher resistance to pressure and - conical nipple and valve body seat of abrasion armatures - insulations for electric machinery
    - Better heat conductance - starting disc

Limits of application: only partly resistant to alkalines and acids, resistant against organic solvents

- **carbon**
    - High resistance to pressure and hardness - Construction parts with antistatic requirements
    - Good slip properties and resistance to - friction bearing, valve box, valve body abrasion seat for the chemical applications
    - Good heat conductance engineering

    - Low volume- and surface resistance - Piston seal-/guiding elements dry operating compressor
    - Radial Shaft Seal

Limits of application: Depending on carbon grade e.g.brittle, abrasion by oxydizing media

- **carbon fibers**
    - Very low cold flow - friction bearing
    - Good resistance to abrasion, coating of rolls, good electric conductivity

- **graphite**
    - Good slip properties and low friction - Slip films for antistatic requirements coefficient
    - Good heat- and electric conductance
    - No static charge

Limits of application: High abrasion with hard metals/reverse device, abrasion of filler by strongly oxydizing media

- **bronze**
    - Good slip properties and abrasion properties - Glide elements in mechanical engineering - High pressure resistance - friction bearing
    - Low cold flow
    - Good heat conductance

Limits of application: Abrasion by acids and water possible [18]

9.1 Processing of PTFE compounds

Basically the same requirements as for Standard S-PTFE are applied for the processing of PTFE compounds. The moulding pressure is the major difference because compounds generally need a higher pressure then unfilled PTFE and for some grades a higher sintering temperature. The maximum temperature for some fillers and filler combinations are processed at 375°C. [9]

In opposite to inorganic fillers, organic fillers are made from natural or synthetic organic materials. They originate from natural materials including wood and shell flours. Synthetic material derived fillers include fluoropolymer spheres and milled polymer waste. These fillers are charaterized by relatively low cost and low density and might increase the flammability and decrease the moisture resistance of plastics. [18]

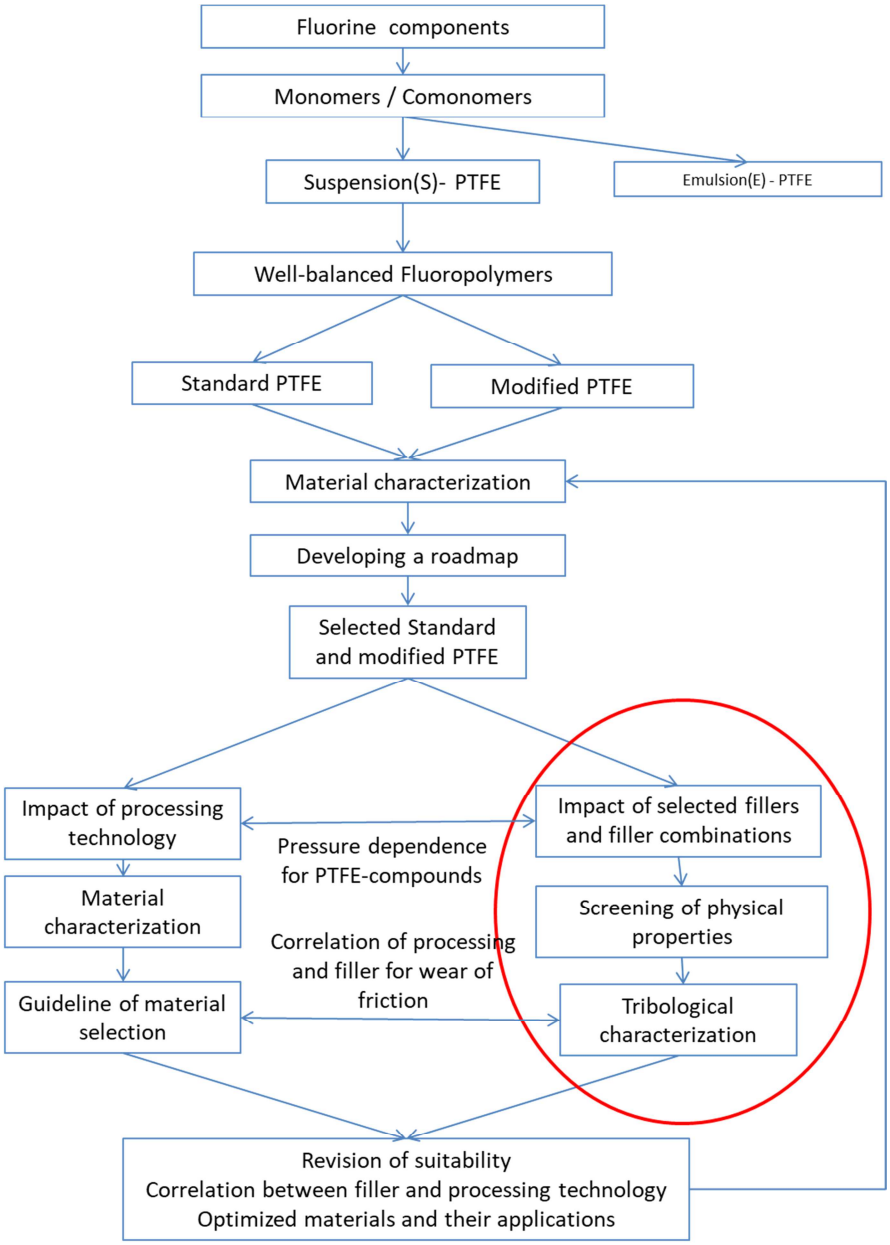


Figure 9-2: Overview of the systematic approach for optimization

In this chapter firstly the impact of the selected fillers and filler combinations on physical and mechanical properties is considered before a screening of physical properties follows to complete this chapter with a tribological characterization.

9.2 Blending with Standard and modified PTFE

First of all the low flow Standard (PTFE-G) and modified PTFE (PTFE-MG-1) which were selected in chapter 7 are blended with organic and inorganic fillers. In total 16 different compounds, composed of one up to three filler combinations are produced in order to get a

systematic overview about the influence of filler combinations on the characteristics of the compound.

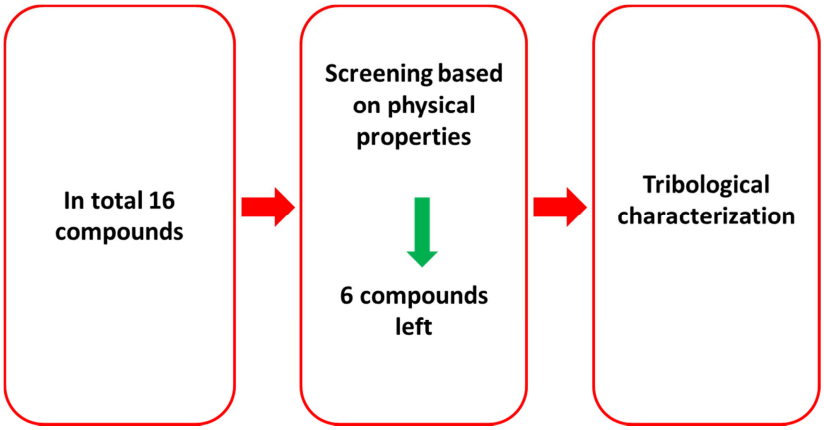


Figure 9-3: Compound screening scheme

As already mentioned the requirements, especially in bearing applications, are low wear, low abrasion, thermal conductivity, reduced COF and cold flow reduction. Those requirements are not only used in bearings, but also in a lot of other important applications these parameters are important. Preferred candidates for fillers and its main benefits are bronze for thermal conductivity, carbon fiber for cold flow reduction, carbon for low wear, HP Polymer for low abrasion, MoS_2 for low COF and graphite also for low COF (Fig. 9-4). This proceeding is important to investigate the different fillers and the requirements in a systematic way. Additionally other fillers and filler combinations, not only for bearings, can be choosen, but in this work fillers for the above mentioned requirements were determined (Tab. 9-2).

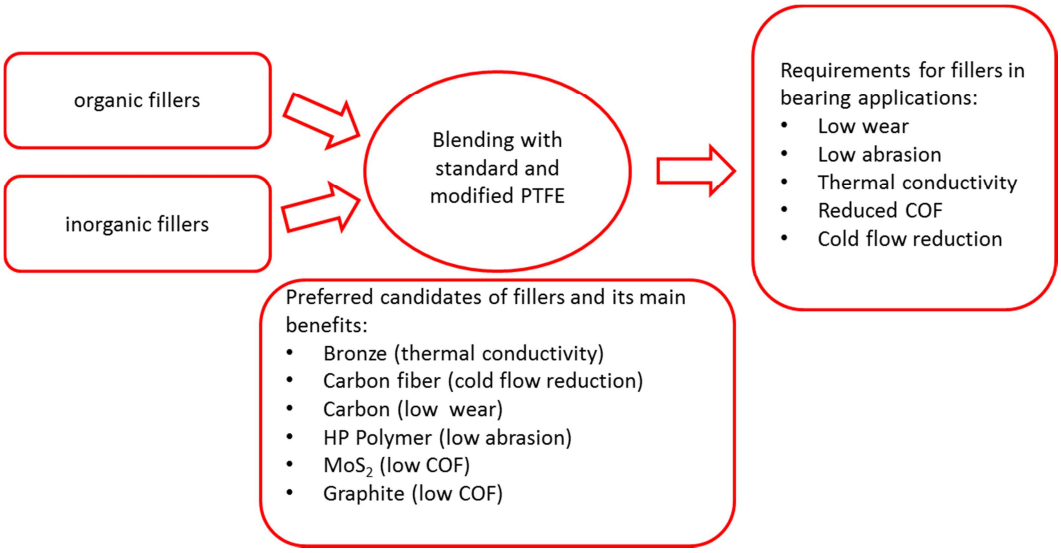


Figure 9-4: Overview of blending

Due to their intrinsic thermal stability, the sintering cycles for organic and inorganic fillers are slightly different. It is recommended to use lower temperatures for holding the plateau (365°C) for organic compounds and sligthly enhanced temperatures (375°C) for inorganic compounds.

No	Resin		Filler 1		Aspect ratio	Filler 2		Aspect ratio	Filler 3		Aspect ratio	Filler content
	Type	%	Type	%		Type	%		Type	%		total in %
1	PTFE-MG-1	69	Glass fiber	27	5,0	MoS_2	3	1,0	Pigment red	1	1,0	31,0
2	PTFE-MG-1	75	Carbon coke	13	1,0	Graphite	12	1,0				25,0
3	PTFE-MG-1	75	Carbon coke	25	1,0							25,0
4	PTFE-MG-1	85	PI	15	1,0							15,0
5	PTFE-MG-1	40	Bronze	55	1,0	MoS_2	5	1,0				60,0
6	PTFE-MG-1	73	PPS	15	1,0	Carbon coke	10	1,0	MoS_2	2	1,0	27,0
7	PTFE - G	73	PPS	15	1,0	Carbon coke	10	1,0	MoS_2	2	1,0	27,0
8	PTFE-MG-1	60	Bronze	30	1,0	CF	10	3,0				40,0
9	PTFE - G	60	Bronze	30	1,0	CF	10	3,0				40,0
10	PTFE-MG-1	83	CF	10	3,0	Graphite	5	1,0	Arom.Pol.	2	1,0	17,0
11	PTFE - G	83	CF	10	3,0	Graphite	5	1,0	Arom.Pol.	2	1,0	17,0
12	PTFE-MG-1	89	$PPSO_2$	10	1,0	MoS_2	1	1,0				11,0
13	PTFE-MG-1	79	CF	10	3,0	Graphite	10	1,0	TiO_2	1	1,0	21,0
14	PTFE-MG-1	85	CF	10	3,0	Polyimide	5	1,0				15,0
15	PTFE-MG-1	80	CF	10	3,0	Polyimide	10	1,0				20,0
16	PTFE - G	80	CF	10	3,0	Polyimide	10	1,0				20,0

Table 9-2: Overview of selected compounds

9.3 Screening of physical properties

The main target for the screening of the physical properties screening is to analyze the results and select the best fillers. Therefore the measurements of density, shrinkage, tensile strength and tensile elongation are considered before the tribological screening is done. The combination of different specific values is important.

9.3.1 Density measurements

The density of a PTFE moulding measured at room temperature following a standard fabricating cycle (standard specific gravity, SSG) is a suitable criteria for the characterization of the molecular weight of PTFE. The SSG is reduced when the samples have a very high molecular weight in relation to those having relatively low molecular weight. This dependence comes from the fact that the rate of crystallization and consequently the crystallinity of melt-crystallized PTFE varies inversely with molecular weight in a certain range. [52]

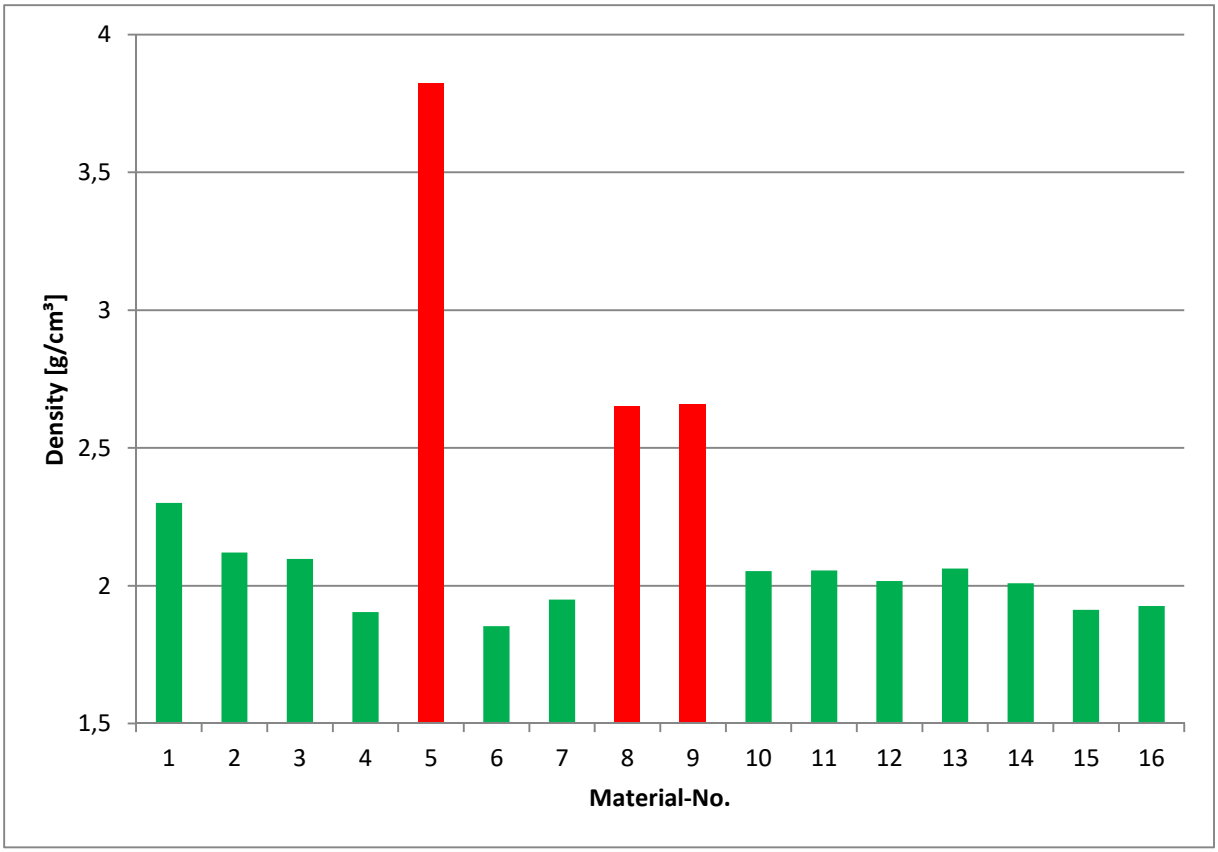


Figure 9-5: Density measurements for different compounds

The density measurements in figure 9-5 show the highest results for material No. 5, 8 and 9. The reason for this is the bronze filler. The other materials are much lower and the differences are not extremely distinguished.

9.3.2 Analysis of tensile properties

Obviously it is not adequate to eliminate a material only because of the tensile strength and other variables has to be considered - but it is an indication. The kind of stress in real applications are different. For example, if results for tensile strength are worse, mechanical failure at higher load can occur. Decreased results in tensile elongation can generate problems in manufacturing and installation process. Internal stresses in the material are effected by the shrinkage. So the measurement results are important for working processes, but for a final selection all results have to be considered.

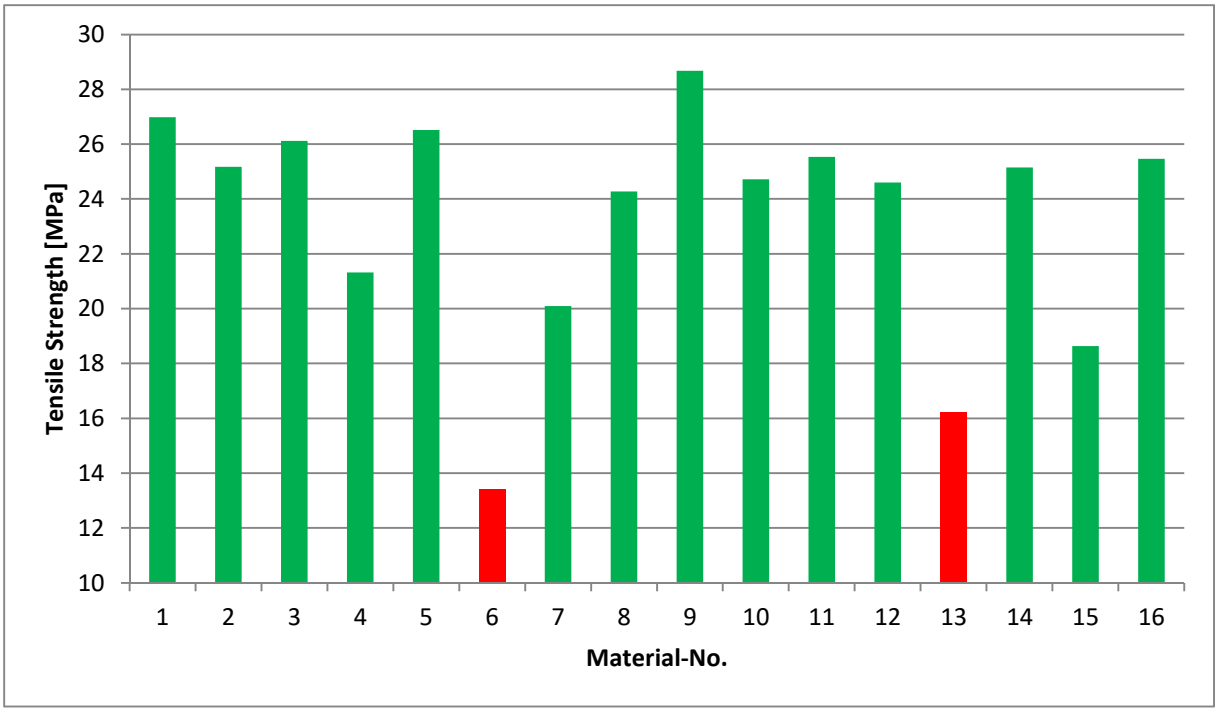


Figure 9-6: Tensile strength for different compounds

In figure 9-6 the material No. 6 and 13 have the lowerst tensile strength, although both materials are modified materials. Material No. 6: The content of the three fillers in total is 27wt-%. As the main filler is an organic substance with low SSG, the overall vol-% exceeds 50%. Thus the share of PTFE within the compound is significantly reduced resulting in poor mechanical properties. The compounds with low physical strength are not acceptable for high strain so that material No. 6 and 13 are not appropriate for applications with required good mechanical properties. The other materials have much higher results especially No. 1, 5 and 9, an additional reason for choosing them for the tribological characterization.

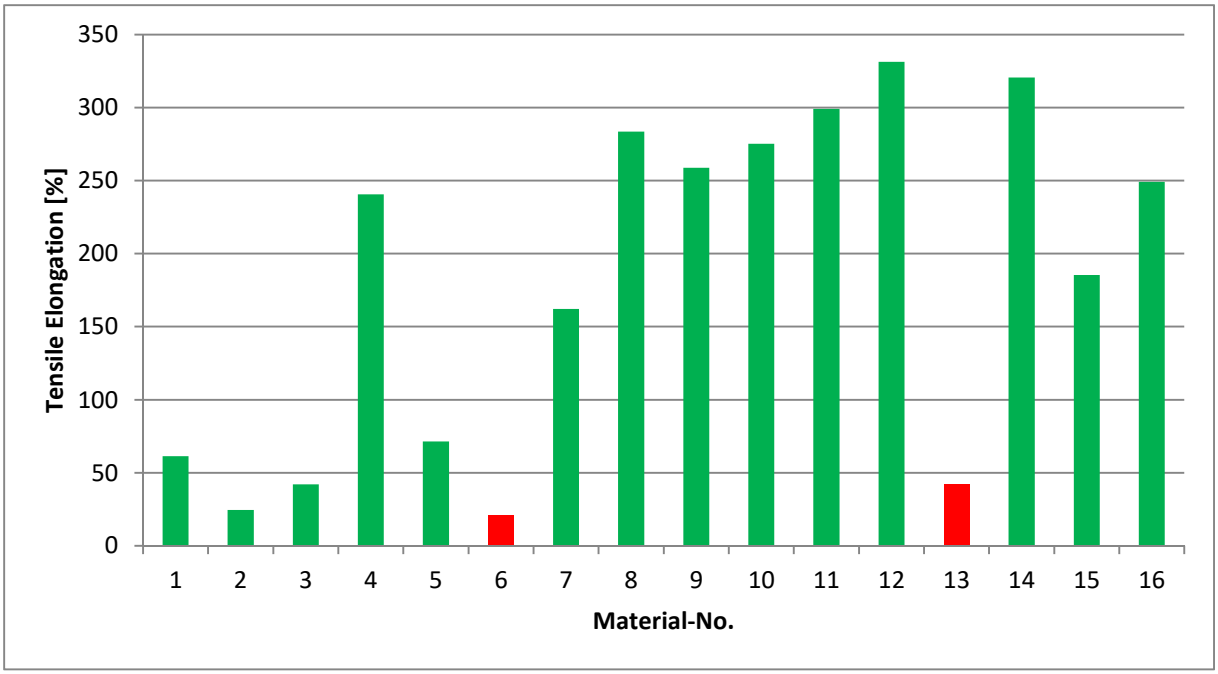


Figure 9-7: Tensile elongation for different compounds

This lower tensile strength results are confirmed by the results of tensile elongation. Also here the materials No. 6 and 13 have the lowest results (Fig. 9-7). It can be said, that low elongation is a disadvantage for the manufacturing and assembly process and recovers the danger of crack formation at impact load. So this characteristic is not a criteria of elimination in general, but the manufacturer needs to work with those difficulties of possible crack formations.

9.3.3 Shrinkage measurements

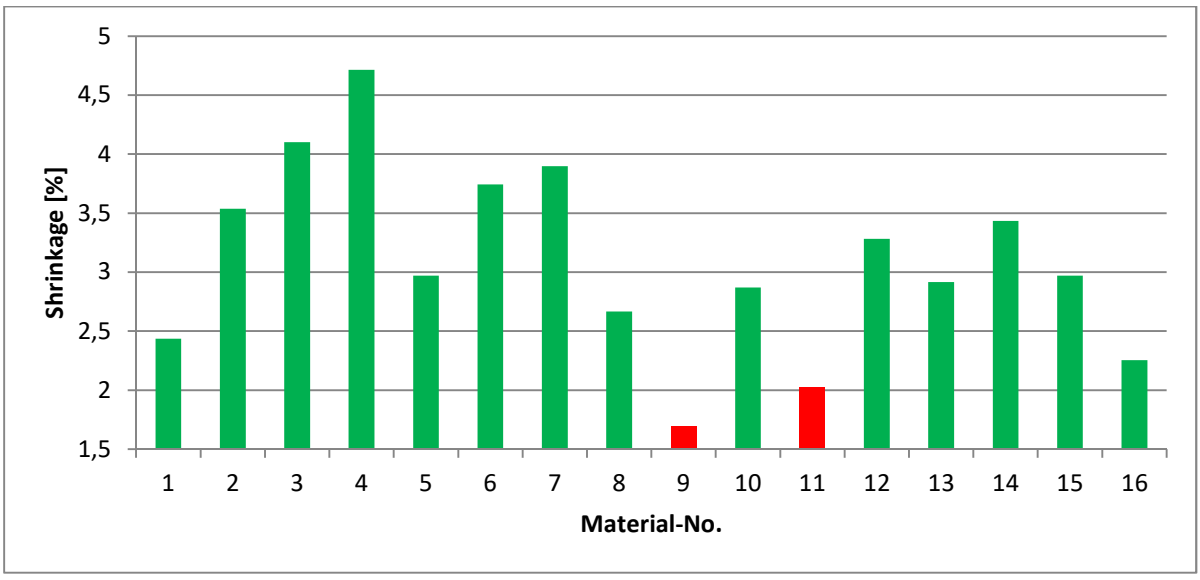


Figure 9-8: Shrinkage for different compounds

The lowest shrinkage results have materials No. 9 and 11 (Fig. 9-8). Both basic materials are Standard PTFE in connection with carbon fiber and other fillers. A low shrinkage behaviour during sintering is advantageous for the manufacturing of stress-relieved components. Material No. 4 has the highest shrinkage, but only one filler. The results for material No. 6 and 13 are good. Although material No. 10 (Standard) has the same filler as No. 11, it has a higher shrinkage, but still acceptable – the reason why this material was choosen anyway for tribological characterization.

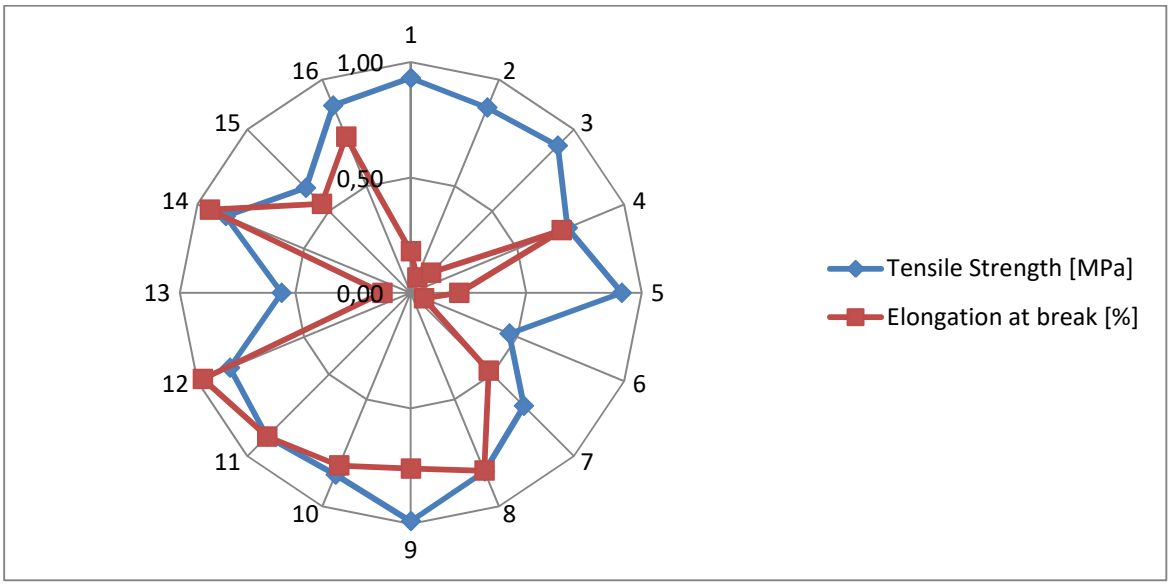


Figure 9-9: Tensile strength and elongation at break for different compounds

As already mentioned and shown in figure 9-9 the tensile strength for materials No. 1, 5, 9, 10 and 14 have the highest result, but also the other compounds have good results. More striking are the results for the elongation at break for the different materials. In comparison materials No. 1, 2, 3, 5, 6 and 13 are extremely low, although they are all modified PTFEs. The best results for elongation at break have materials No. 12 and 14 with completely different fillers.

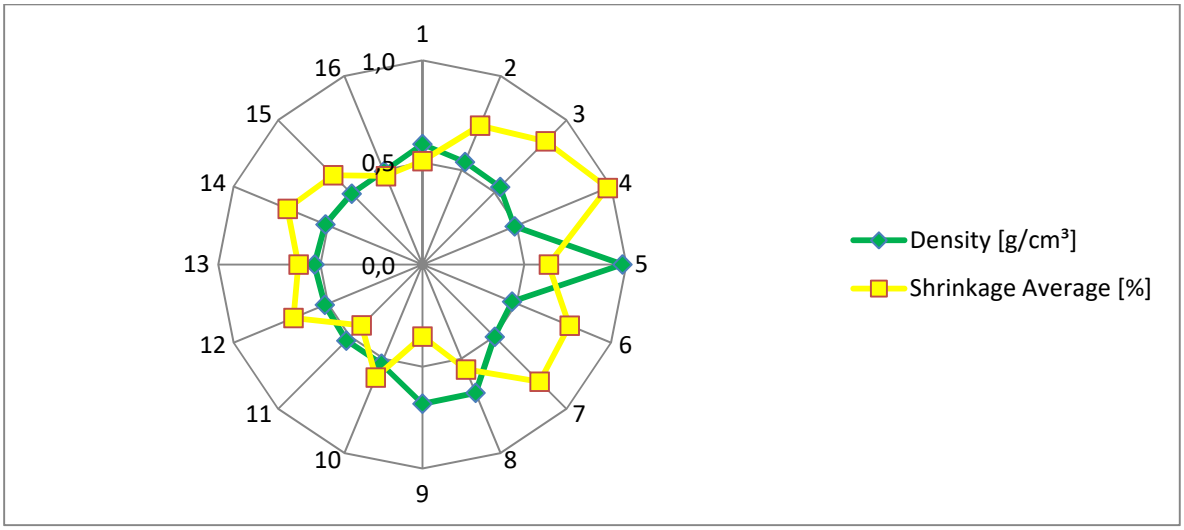


Figure 9-10: Density and shrinkage for different compounds

Figure 9-10 shows material No. 4 with the filler Polyimid has the highest shrinkage of all materials, while materials No. 9 and 11 have the lowest. As already mentioned the bronze compounds have the highest shrinkage. Therefore they are subject for higher internal stresses generated during sintering.

9.3.4 Thermogravimetric Analysis

For thermal analysis some techniques are included like DSC, DTA, TGA, DMA and DMTA. Advantages over other analytical techniques of thermal analysis are variablity with respect to application of thermal energy, small sample size, the material can be in any solid form – gel, liquid, glass, solid, ease of variability and control of the sample preparation, ease and variablity of atmosphere, it is relatively rapid and instrumentation is moderately priced. Mostly, and also in this work, the thermal analysis data are used in combination with results from other techniques. [26]

Using TGA means a continuous control of weight of the polymer as it is subjected to a temperature program of temperatures up to 1000 °C. Quantitative informations about the kinetics of the thermal decomposition of polymer materials from which the thermal stability can be evaluated are staged in this technique. Factors such as the effect of crystallinity, molecular weight, orientation, tacticity, substitution of hydrogen atoms, grafting, copolymerization and addition of stabilisers on polmyer degradation can be pictured. [18]

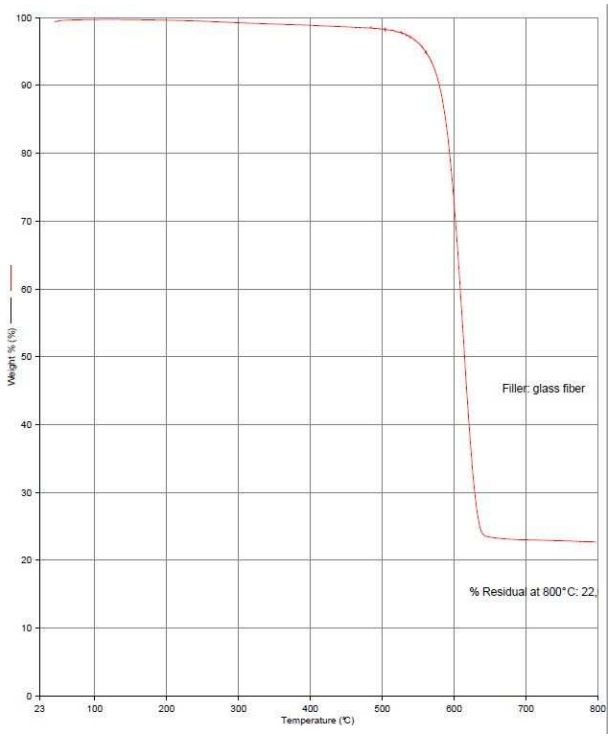


Figure 9-11: Example of a TGA curve for PTFE + 23wt-% glass fiber

A wide range of polymer characteristics can be determined by TGA such as:

- Weight loss measurements and water or volatile contaminates
- Chemical composition
- Thermal stability
- Polymer degradation or decomposition
- Determination of activation energy (E)
- Polymer transition studies
- Effect of antioxidants on ageing
- Polymerization kinetics
- Combustion inhibition studies
- Polymer life determination
- Effect of catalysts
- Copolymer composition
- Additive degradation studies [49]

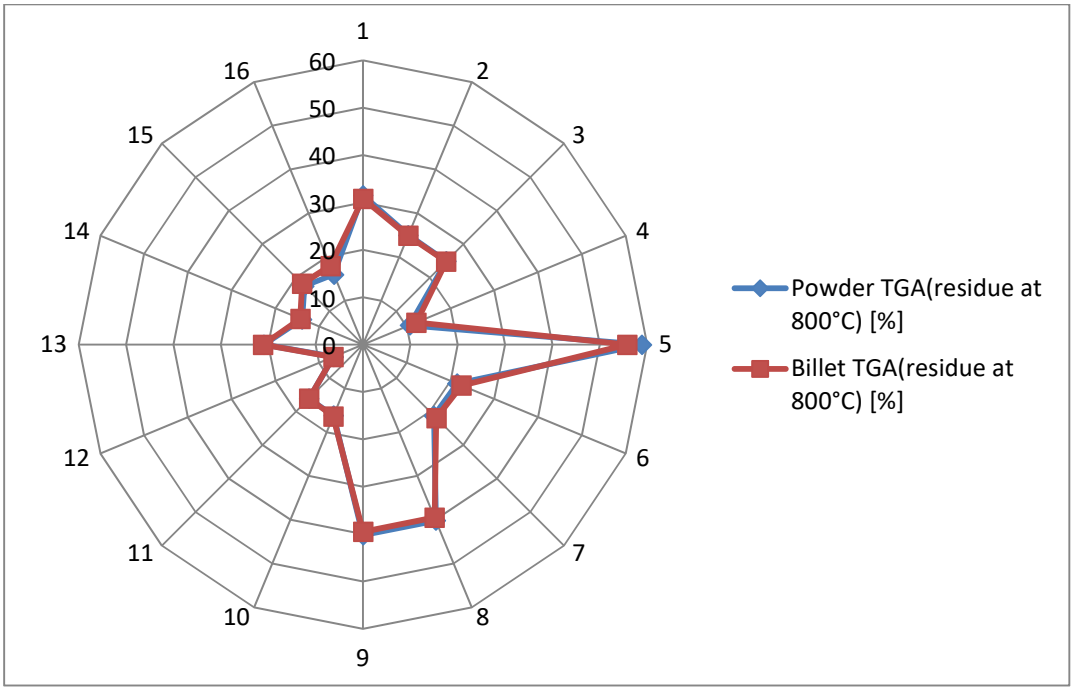


Figure 9-12: TGA measurements for powder and billets of compounds

In this study the TGA is done for the compounds to a temperature up to 800°C on the one hand for the powder, and on the other hand for the finished billet. There are no significant differences between these measurements. But the results of the different materials show, that material No. 5 has the highest result of all materials. Also the materials No. 8 and 9 show higher values (Fig. 9-12).

9.3.5 Selection of compounds because of physical properties

After the evaluation of physical properties of all 16 compounds and their fillers a selection of at least 6 compounds is made for determination of the tribological properties. The major benefits are demonstrated in figure 9-13 below. The materials are well-balanced regarding Standard and modified PTFE and the different fillers with their different properties.

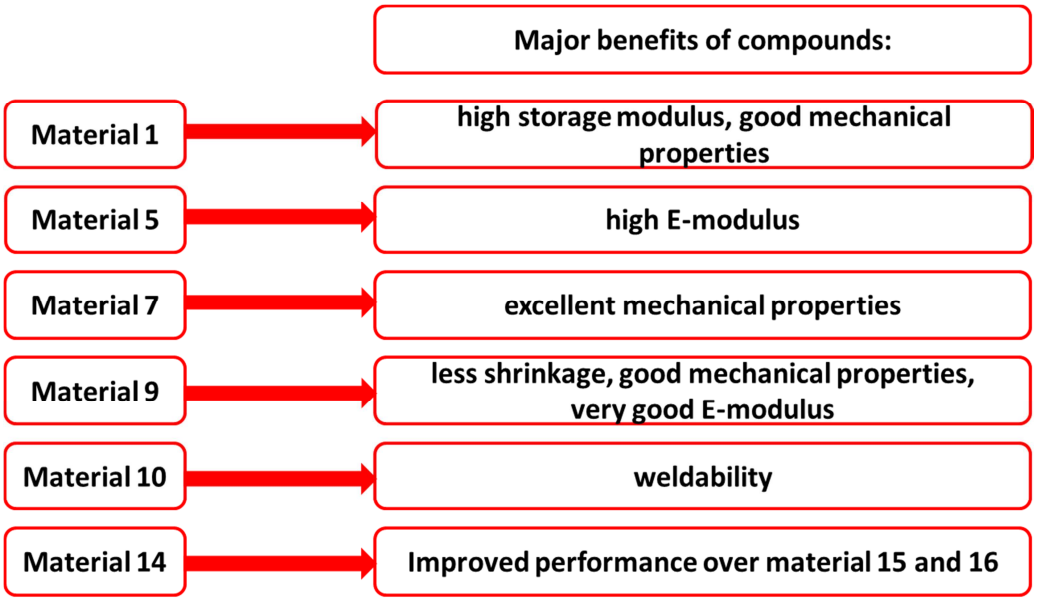


Figure 9-13: Selection of compounds for certain applications with their specific physical properties [50]

Materials No. 7 and 9 are based on Standard PTFE whereas the other materials are related to modified materials. In general all these materials have excellent mechanical properties which is important for most applications. Material No. 10 is, beside this, choosen because of the weldability of the modifier PPVE, although the mechanical properties are not outstanding.

9.4 Tribological characterization

To characterize the friction and wear properties of tribological systems there are many ways. The most common approach is to determine appropriate values for the coefficient of friction and the wear rates under specific values for contact pressure and friction speed. In addition to the physical properties the tribological characterization is a good supplement for materials.

9.4.1 Concept of tribological tests

In this work especially bearings for two applications as testing cases are determined. Home improvement market, like the drilling machine with maintenance free bearings and leisure mobility, like bearings in racing bikes are focussed. The major targets are maintenance free use, weight reduction and reduced cost-of-ownership.

Different concepts for material selection can be targeted, but in this work, for tribological compound screening only accelerated live time tests at elevated PV-values are applied. For the first tests it is a PV-value of 4.42 (N/mm^2* m/s) with on the one hand P(max):

4.42 N/mm^2 and V(max): 1 m/s and on the other hand P(max): 2.21 N/mm^2 and V(max): 2 m/s. For illustration exemplified two different applications are targeted:

Racing bike with PV-value in the range of 0.16 – 0.29 (N/mm^2 * m/s), where P_{sit}: 0.9 N/mm^2, V_{sit}: 0.18 m/s and P_{stand}: 6.0 N/mm^2 and V_{stand}: 0.05 m/s

Drilling machine at about PV-value 0.6 (N/mm^2 * m/s), where P: 0.29 N/mm^2 and V: 2.0 m/s. Pin disk tests are done for informations about the wear, the wear rate, the coeffiction of friction and the temperature course behaviour.

9.4.2 Pin disk evaluation

For pin disk evalutation the test load for the first tests is 500 N with a friction speed of 1 m/s. The test specimen has a diameter of 12 mm and a height of 10 mm. As already mentioned above the resultant PV-values is 4,42 (N/mm^2 * m/s) with a temperature range of the specimen holder of about 40 – 120°C. The surface of the counter part is 42CrMo4, grinded and hardened to 60 HRC. At this measurements following values are distinguished:

- Test load
- Friction speed
- Temperature (at the back of the test specimen)
- Friction torque
- Coefficient of friction (through test load and friction torque)
- Total wear (approximation of specimen holder of mating surface)
- Determination of abrasion of mating surface: characterization through surface scans before and after test

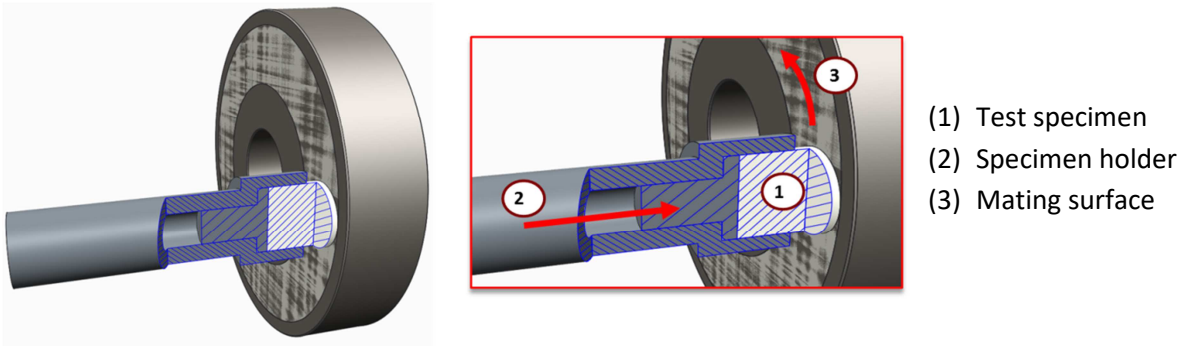


Figure 9-14: Pin disk test- built up [20]

As it can be seen in figure 9-14 the test specimen (1) is fixed with the specimen holder (2), which is also the application of load and the mating surface (3). For the test sequence 15 min static strain is done with a 4 – 5 hour load and friction speed.

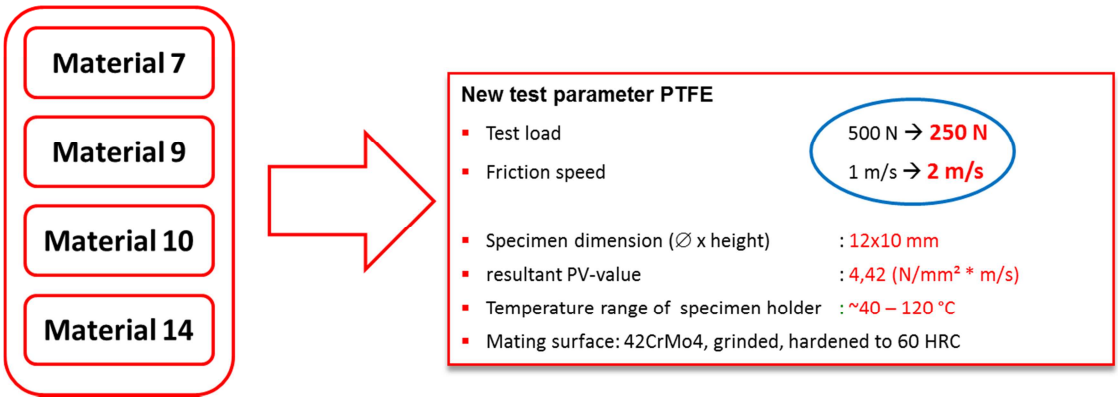


Figure 9-15: Adjusted test parameters with reduced load at higher speed [50]

After the first tests are finished two materials are eliminated because of the wear rate behaviour and four materials are left with changed parameters of a test load of 250 N and a friction speed of 2 m/s (Fig. 9-15).

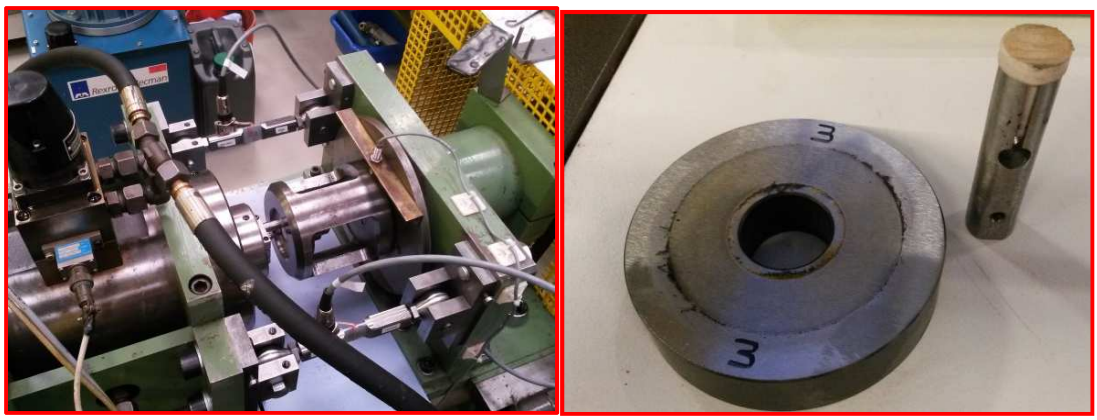


Figure 9-16: test setup with load regulation unit, impulse unit, pin/disk, test specimen and mating surface [20]

9.4.3 Test results of tribological screening

Material-No.	Test load	Friction speed	Total wear [µm]	Coefficient of friction	Characteristics
1	500 N	1 m/s	120	0,58 - 0,63	thermal discolouring
5	500 N	1 m/s	1400	0,35	exceeding wear
7	500 N	1 m/s	260	0,52	short-time increase of wear rate after 60 min.
7	250 N	2 m/s	80 - 140	0,7 (0,4)	
9	500 N	1 m/s	260	0,34	irregular increase of wear rate
9	250 N	2 m/s	20 - 40	0,5 (0,2)	"negativ wear" / deformation of the specimen
10	500 N	1 m/s	80	0,05 - 0,25	"negativ wear" / deformation of the specimen
10	250 N	2 m/s	50 - 70	0,4	"negativ wear" / deformation of the specimen
14	500 N	1 m/s	80	0,42 (0,15)	irregular increase of wear rate in combination with at the same time low coefficient of friction
14	250 N	2 m/s	20 - 70	0,4 - 0,6	"negativ wear" / deformation of the specimen

Table 9-3: Results of tribological tests performed at selected compounds using two different set of conditions resulting in the same P-V-value: 500 N/ 1m/s and 250 N / 2 m/s

The above Table 9-3 summarizes the results of the pin/disk tests. Whenever the results for total wear or coefficient of friction differ in a broad range throughout the test duration, average values are taken for the purpose of preliminary differentiation between the candidates. It also turns out that 500 N loading generated too much contact pressure for some of the softer compounds and irregular test behaviour was the output. Therefore, a second test series is started applying 250 N only. In order to keep the PV-value at the same level, the speed is doubled in the second test series.

In figure 9-17 to 9-22 below the detailed results are described. For the materials No. 1 and 5 the obtained curves for wear and wear rate as well as for coefficient of friction and temperature, both as a function of time, are shown. For these tests the test load is 500 N with a friction speed of 1m/s, while for materials No. 7, 9, 10 and 14 additionally the test load of 250 N and friction speed of 2m/s is pictured. Further interpretation of the results will be subject of a separated project.

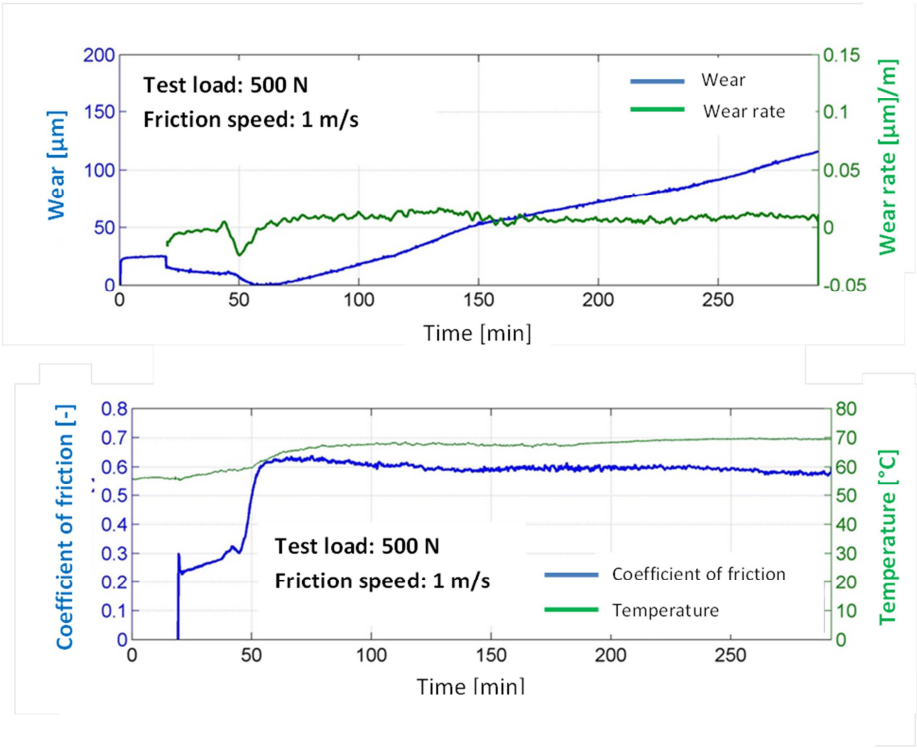


Figure 9-17: Material No. 1 PTFE-MG1 + 69% glass fiber + 3% MoS_2 + 1% pigment red [20]

The elimination reason is for material No. 1 the thermal discolouring and for material No. 5 an exceeding wear as seen in figure 9-17 and 9-18.

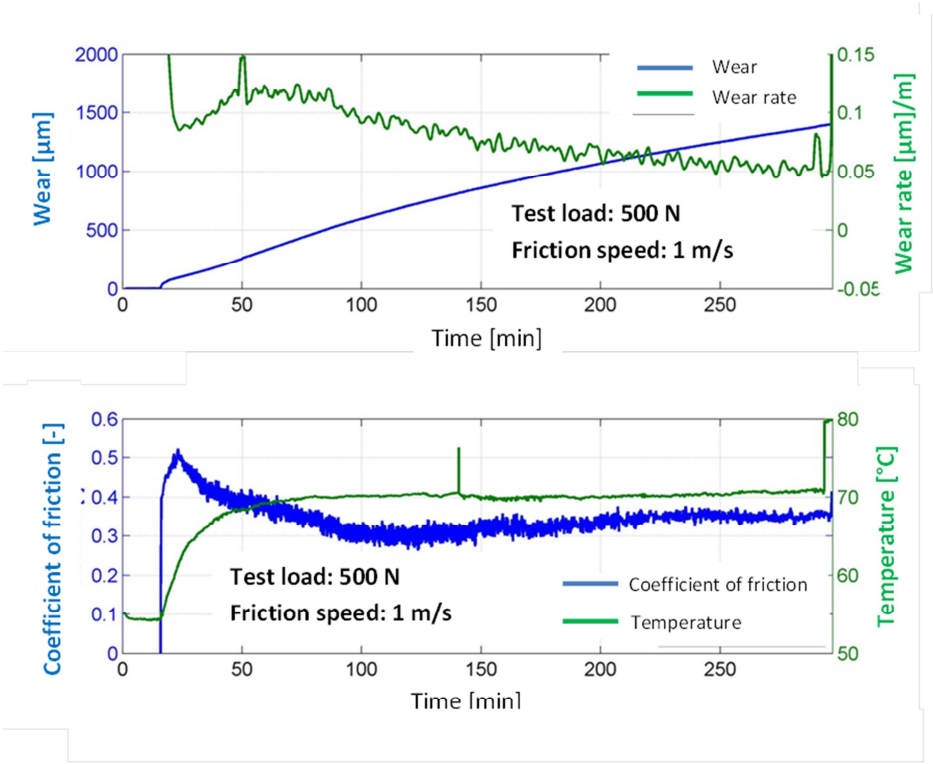


Figure 9-18: Material No. 5 PTFE-MG1 + 40% bronze + 5% MoS_2 [20]

Material No. 7 (Fig. 9-19) has a short time increase of wear after 60 min at a test load of 500 N and a friction speed of 1 m/s with a total wear of 260 µm and a coefficient of friction of 0.52. With changed parameters of test load 250 N and friction speed 2 m/s the total wear decreases in the range of 80 – 140 µm, while the coefficient of friction increases to 0.7.

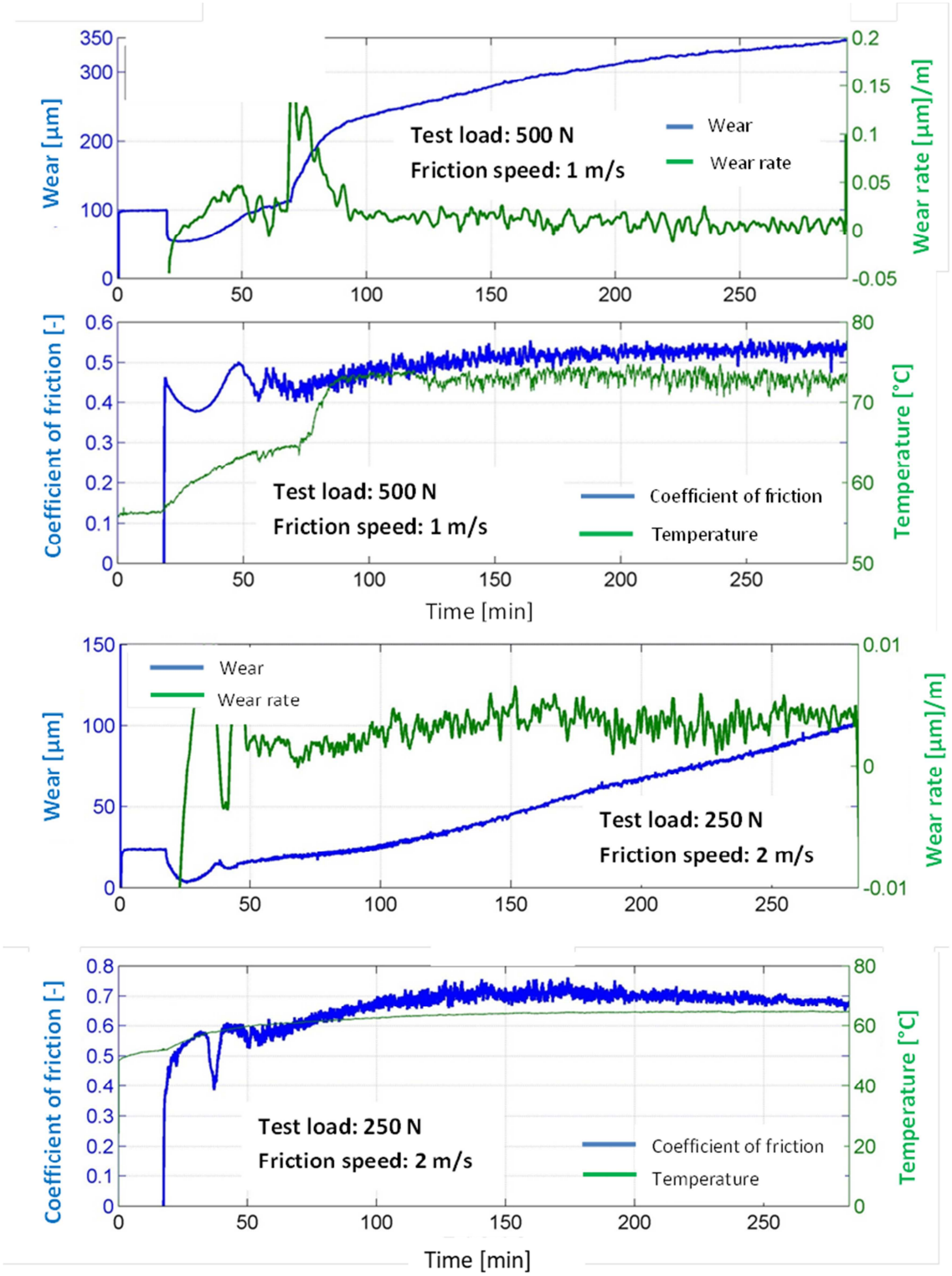


Figure 9-19: Material No. 7 PTFE-G + 15% PPS + 10% Carbon Coke + 2%MoS_2 [20]

Material No. 9 (Fig. 9-20) has an irregular increase of the wear rate at 500 N and 1 m/s with a total wear of 260 µm and a coefficient of friction of 0.34. In comparison to this test at 250 N and 2 m/s the total wear is lowered to 20 – 40 µm and the coefficient of friction increases to 0.5. The specimen show a negative wear including deformation.

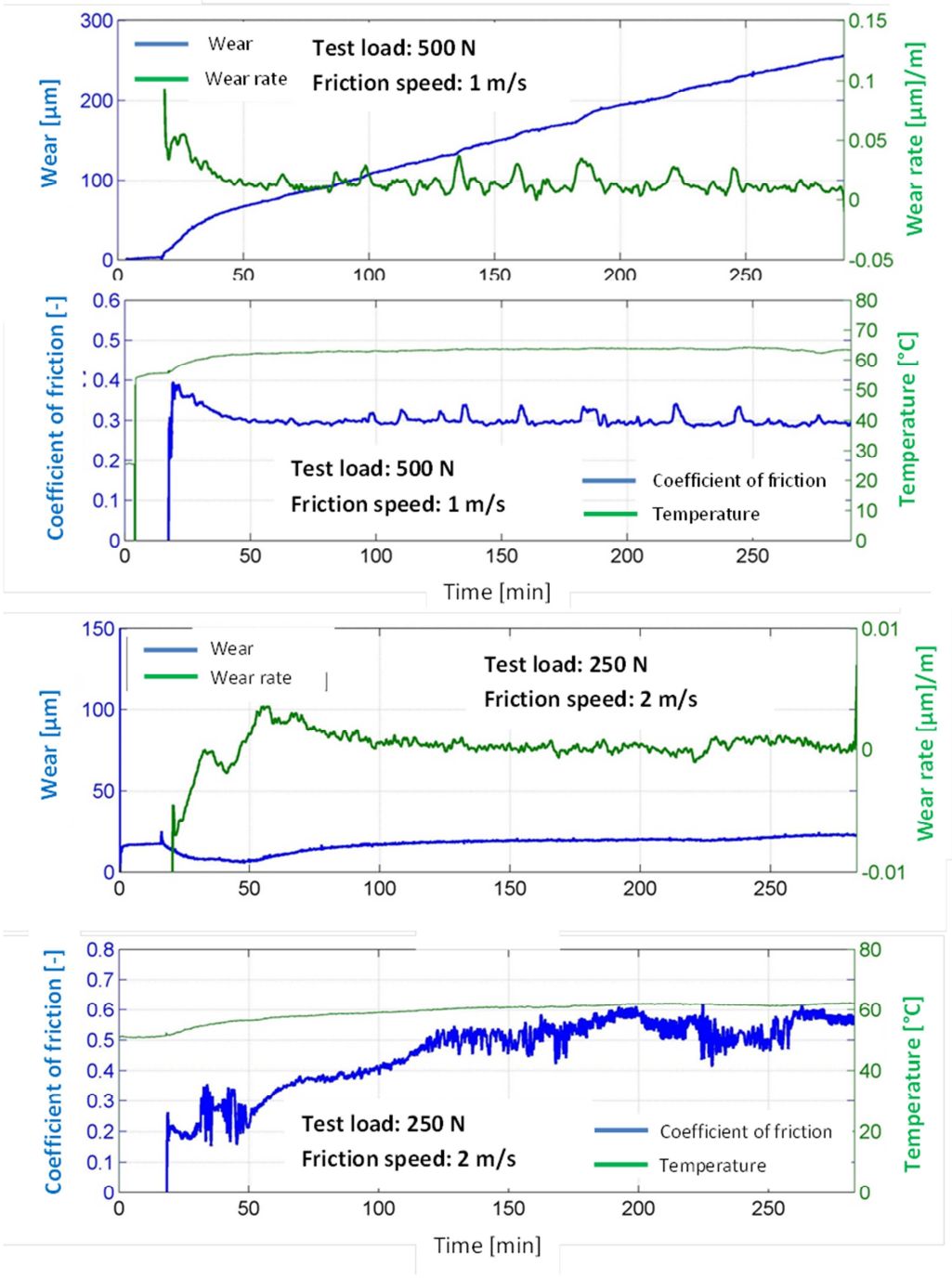


Figure 9-20: Material No. 9 PTFE-G + 30% bronze + 10% carbon fiber [20]

Material No. 10 (Fig. 9-21) has, as well at 500 N and 1 m/s and 250 N and 2 m/s, a negative wear and a deforming of the specimen.The total wear decreases with decreasing test load from 80µm to the range of 50-70 µm. The coefficient of friction increases with higher speed from the range of 0.05 – 0.25 to 0.4.

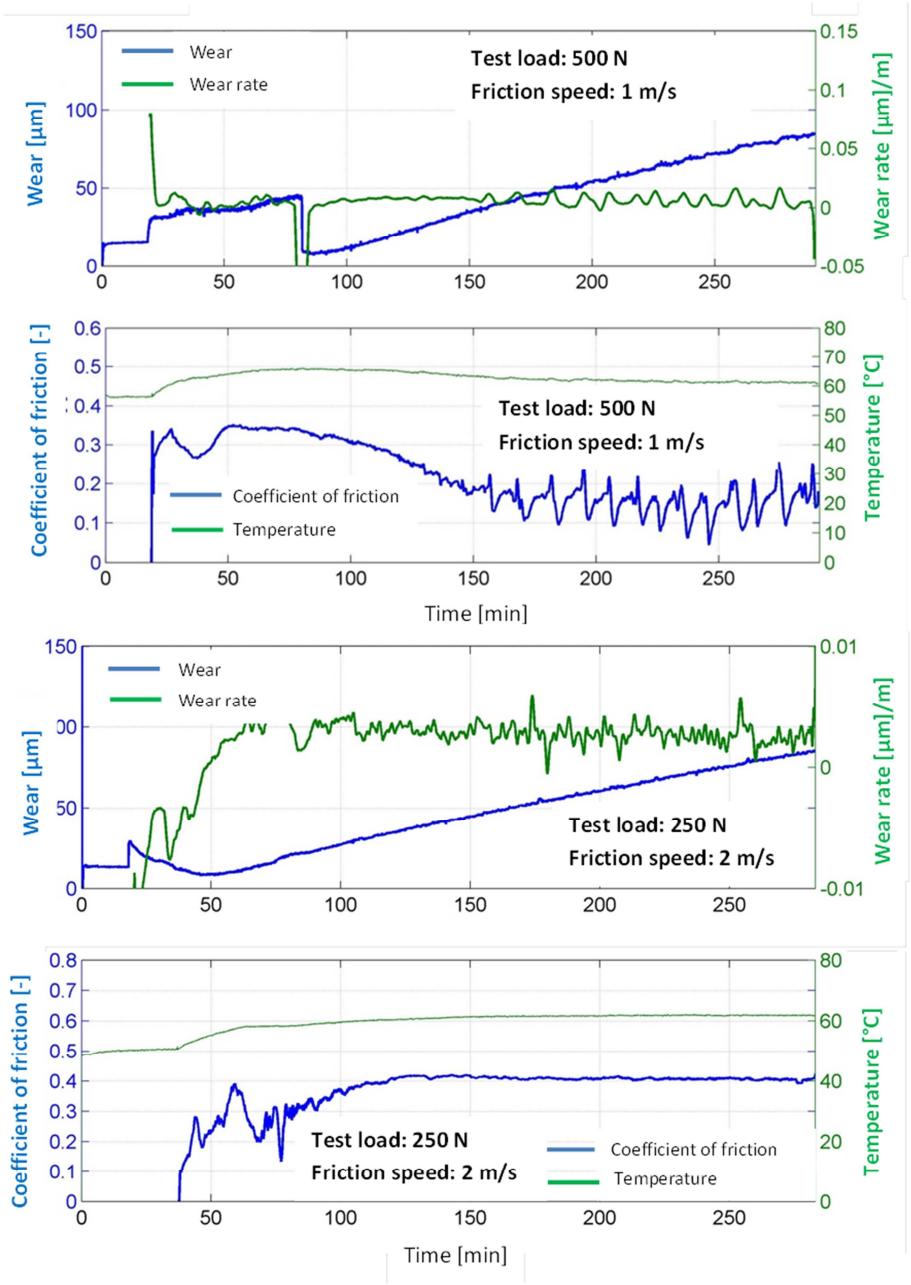


Figure 9-21: Material No. 10 PTFE-MG1 + 10% Carbon fiber + 5% Graphite + 2% Arom. Pol. [20]

Material No. 14 (Fig. 9-22) at 500 N and 1 m/s has a wear rate of 80µm and a coefficient of friction of 0.42 whereas the wear rate decreases with decreasing load to 20 – 70 µm and increasing coefficient of friction in the range of 0.4 – 0.6. At 500 N the coefficient of friction is changing periodicly with peaks towards lower values. The origin may be a periodic replacement of the film transfer. This hypothesis is supported by the stepwise increase wear. At 250 N the specimen is deforming with a negative wear.

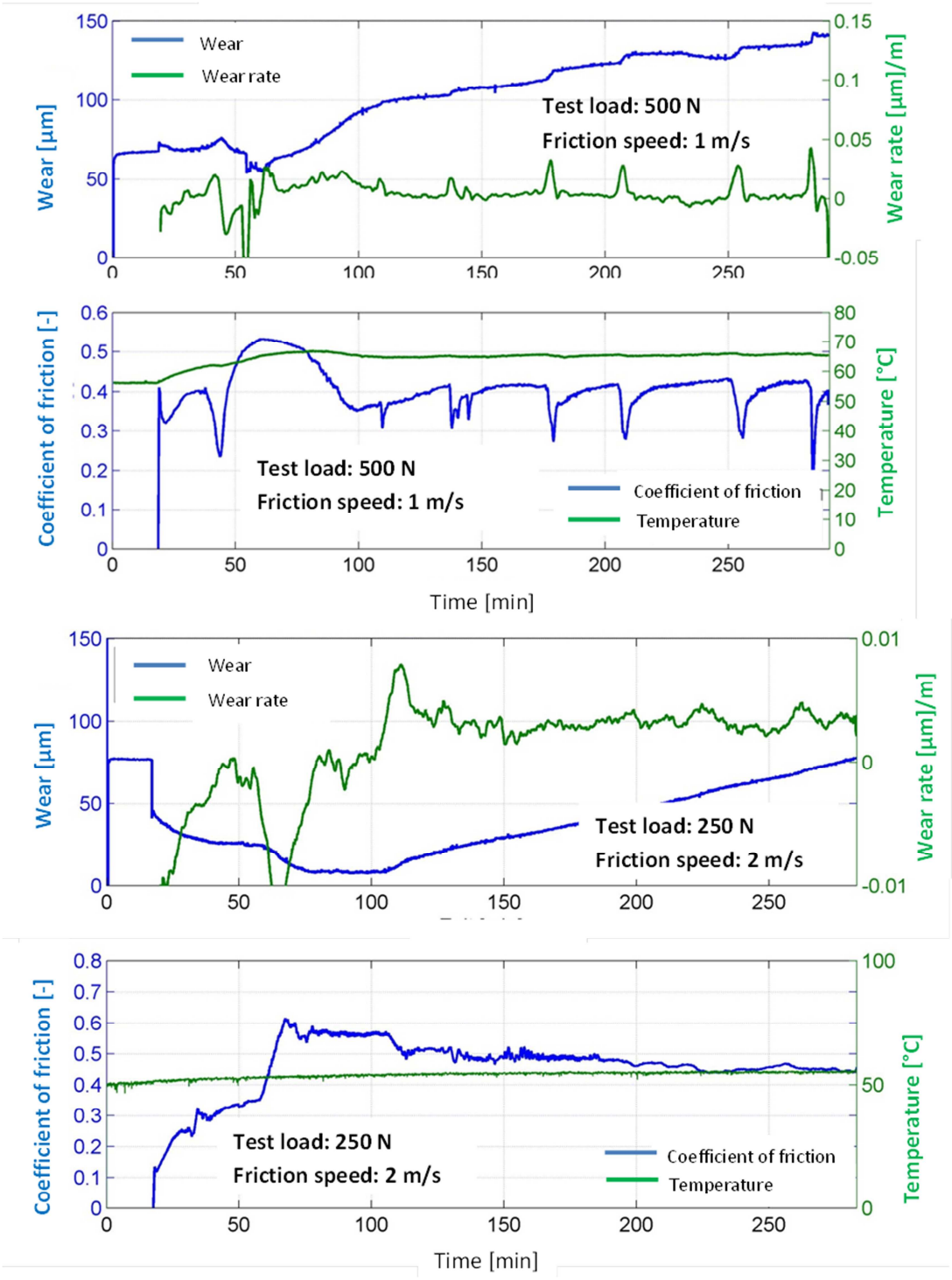


Figure 9-22: Material No. 14 PTFE-MG1 + 10% Carbon fiber + 5% Polyimide [20]

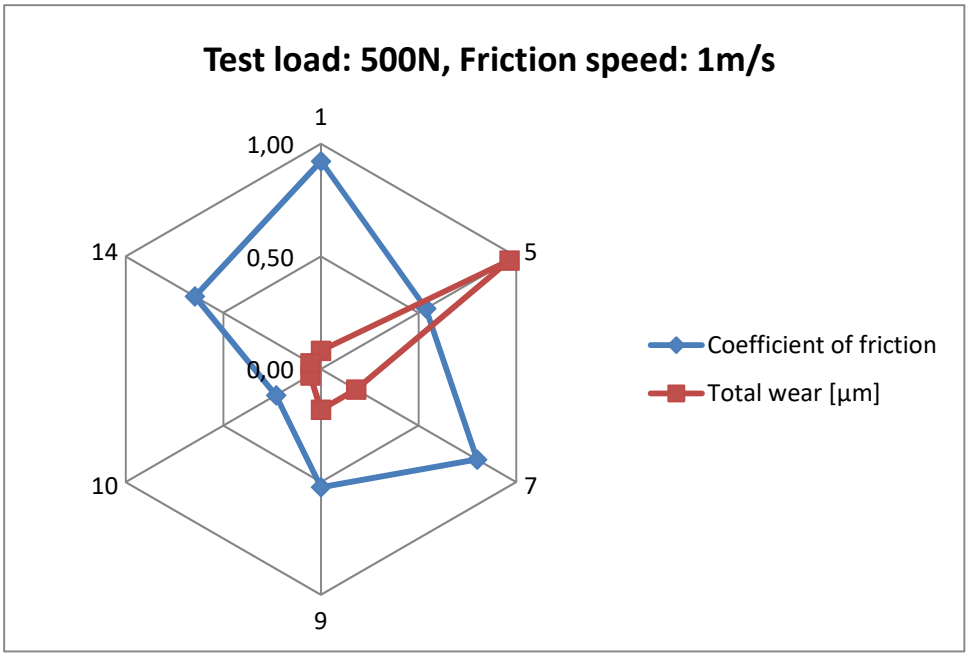


Figure 9-23: Coefficient of friction and total wear for first tests

In comparison the 6 materials in figure 9-23 it can be seen, that material No. 1 has the highest coefficient of friction and material No. 5 the highest total wear, why these materials are not adapted in the applications that are named in this work. Of course anyway for other applications it is possible to use these compound materials.

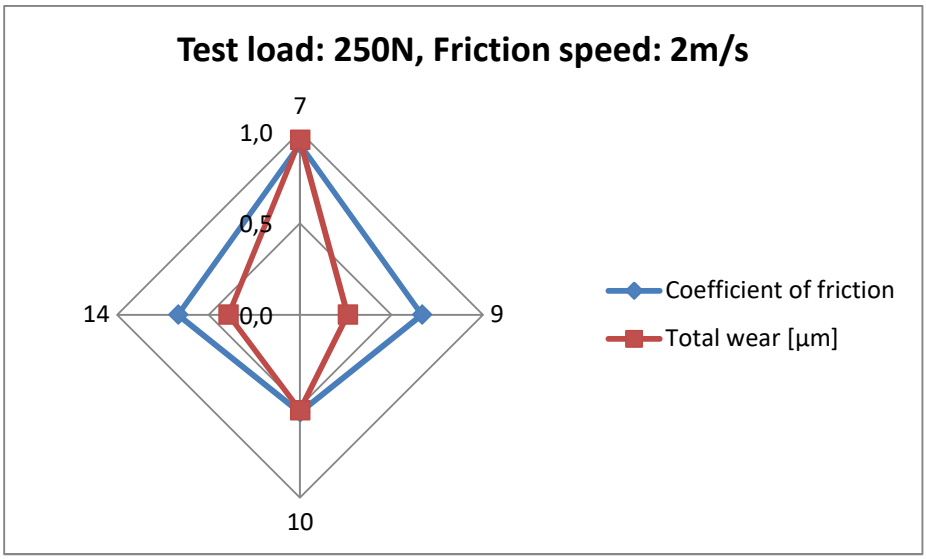


Figure 9-24: Coefficient of friction and total wear for secondardy tests

The findings for the test parameter adjustments are that the best results are for material No. 7 which is an organic filler with a high wear resistance and a reduced COF. Another result is that enhanced PV-values generate additional failure mechanism. Additional tests are required at lower PV-values to fill the gap between initial accelerated tests and final target PV-values. [50] This additional tests should be done in future, based on the philosophy described in this work.

10 Summary and Conclusions

After evaluation of all materials again the overview gives a clear view of the recommended practice to find the optimized material for each application.

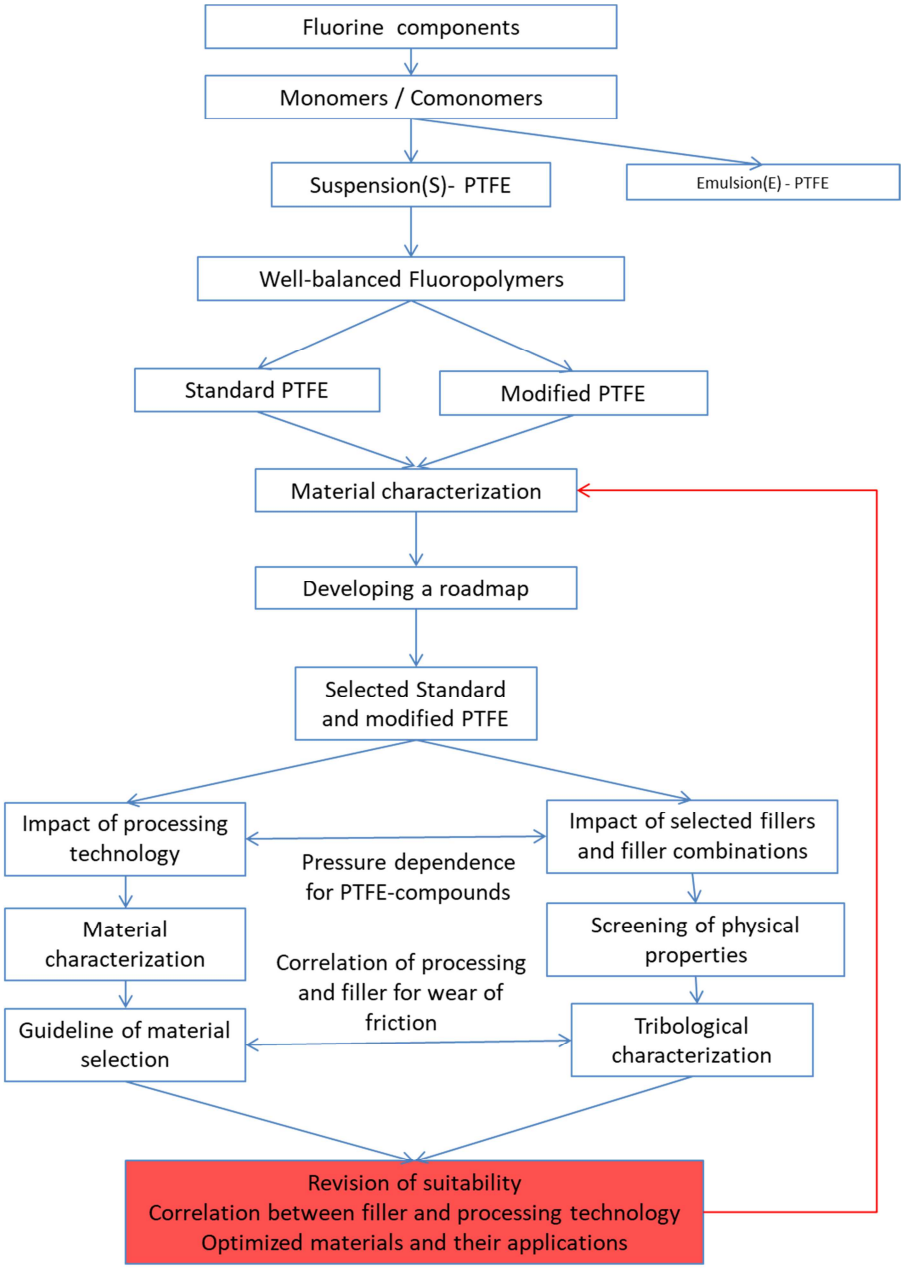


Figure 10-1: Overview of the systematic approach for optimization

As Figure 10-1 above shows, after the material characterization of the PTFE itself, the processing technologies and the tribological characterization of compounds, a revision of suitability has to be done and the correlation between the filler and the processing technology must be respected. If the suitability or the correlation is not fitting for the favoured application it is recommended to return to the material characterization of the PTFEs to find the best solution. By using this systematic way every user can find the optimized material for nearly every application.

In this work applications for home improvement and leisure sports are analyzed in detail by a tribological characterization. But as already mentioned it is of course possible to use this systematic way for other applications like following examples:

- In the chemical industry, especially compounds with modified PTFE are used in order to reduce creep in gasket application
- The addition of a conductive pigment generates an electrostatic decipatice property for safe applications in contact with non aqueous lubricants
- For ball valve seat rings two components are preffered: modified PTFE + 25% glass fiber or + 25% carbon, because of its minimal cold flow and excellent wear resistant properties

Only by a broad knowledge of the different PTFE materials, their properties and the processing technologies in combination with the manufacturing process enables to find the material and process solution. Depending on the targeted applications the required performance profile may be different. In this work all important chemical, physical and mechanical influences are determined and analyzed.

The study of mechanical and thermal behaviour of these materials gives a better unterstanding of the relationship between molecular weight, molecuar weight distribution, particle composition and material properties. A structural investigation were done to show a clear picture of all possiblities to the end performance.

The roadmap in chapter 7 is a guideline for the characterized materials to indicate the differences in mechanical and physical properties. Beside from the important parameters like the molecular weight and particle size and their distribution this roadmap can be used to choose materials for different applications. The choosen Standard and modified PTFE at the end of chapter 7 represent the best fit out of all properties.

Additionally chapter 8 gives a clear view and comparison between the different materials (free flow and low flow) regarding their mechanical properties depending on different moulding pressures and sinter temperatures. Based on this impact of processing technology and the material characterization suggestions for further applications were made.

In chapter 9 the evaluation of physical properties of all 16 compounds and their fillers and after that a selection of at least 6 compounds was made for determination of the tribological properties and the major benefits. The materials are well-balanced regarding molecular weight, molecular weight distributioin and filler incorporation.

By utilising this processes the following conclusions are made:

- The particle size and the weight percentage of the d_{10}-fraction of the material are specific for each material type. The increased specific surface enables an improved coalesence of the particles. In addition, a rough surface compared to a smooth one generates a better surface contact during moulding. Producing compounds will be

done with low flow material because due to the lower particle size the filler distribution is more homogenious.

- In difference to Standard PTFE, modified PTFE has a reduced molecular weight, a reduced cold flow, enhanced mechanical properties and a better melting behaviour during sintering as a consequence of the reduced melt viscosity.
- As a benefit for the processor, PTFE processing is not critical for local pressure variations inside the mould. But lower moulding pressure generates higher shrinkage during sintering.
- Compounds with low phyiscal strength are not acceptable for high strain. It can be said, that low elongation is a disadvantage for the manufacturing and assembly process and recovers the danger of crack formation at impact load. A low shrinkage behaviour during sintering is advantageous for the manufacturing of stress-relieved components.

After testing the samples on the different conditions the best results are obtained for material No. 7 which is a compound composed of Standard PTFE + 15% PPS + 10% Carbon Coke + 2%MoS_2. This compound generates a high wear resistance and a reduced coefficient of friction. Another result is that enhanced PV-values generate additional failure mechanism, especially if the high PV-value is linked to high P-values. Additional tests are required at lower PV-values to fill the gap between initial accelerated tests and final target PV-values.

The comparison of the mechanical and tribological performance of Standard PTFE, modified PTFE and PTFE compounds show the potential of this materials for industrial applications. In general, the mechanical properties of PTFE play an important role for material selection for any applications and can potentially provide new solutions on the fluoropolymer market.

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